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Organic Chemistry of Macromolecules

ORGANIC CHEMISTRY OF MACROMOLECULES

AN INTRODUCTORY TEXTBOOK

A. RAVVE

RESEARCH MANAGER
CONTINENTAL CAN COMPANY

1967

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Preface

This introductory textbook covers the most important and interesting aspects of organic chemistry of macromolecules. It is anticipated that it will be useful in an advanced course in polymer chemistry, assuming that the student has a good background in both descriptive and theoretical organic chemistry. Because it is not assumed that the student has prior knowledge of polymer chemistry, some brief excursions into physical chemistry (kinetics, molecular weight determinations, and so forth) are undertaken to facilitate the discussions.

Organic Chemistry of Macromolecules is also intended as an aid to those organic chemists who did not receive training in polymer chemistry during their graduate studies but now find themselves employed in research efforts in high polymers. Often these scientists are not involved in the physical chemistry of high polymers but need organic chemistry of polymers as a background for their work.

No attempt has been made to present an exhaustive review of the literature. What is offered instead is a selection of references which will present each subject; this was done, of course, in an arbitrary fashion. Also, some information presented is of a speculative nature simply because knowledge on the particular subjects has not fully evolved.

Greater attention is given to synthetic macromolecules than to naturally occurring ones. This is done on the assumption that most organic chemists are more concerned with synthetic materials and also because the natural macromolecules are to a great extent the domain of other fields, for instance, biochemistry.

I would like to express my thanks for encouragement and assistance to my wife, Phyllis.

A. Ravve

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Part I

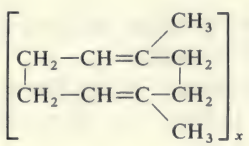
INTRODUCTION

1 Historical Introduction and Definitions

1-1. Historical Introduction

The first proof of the existence of very large organic molecules was supplied by Raoult (*1*) and van't Hoff (*2*), who carried out cryoscopic molecular-weight determinations on rubber, starch, and cellulose nitrate. By the method developed by Raoult (*1*) and by van't Hoff's formulation of solution laws (*2*), molecular weights of 10,000 to 40,000 were demonstrated. Unfortunately, chemists of that day failed to appreciate this evidence and refused to accept it. The main reason for such a response was the inability to distinguish macromolecules from colloidal substances that could be obtained in low molecular weights. The opinion of the majority of that day was that "Raoult's solution does not apply to materials in colloidal state."

During the period 1890–1910 the idea of molecular complexes was generally accepted (*3*). It was used to explain polymeric structures in terms of physical aggregates of small molecules. In fact, molecular association was considered polymerization. Thus rubber, for example, was assumed to be composed of short sequences of isoprene units in either chains or cyclic structures. The structure of isoprene itself was known, because it was isolated from natural rubber in 1860. What added to the general confusion was the fact that no one was able to show the existence of end groups in the macromolecules studied. This enhanced the idea that rubber is a ring-like structure, a dimethyl cyclo-ocatadiene. Large numbers of such rings were assumed to be held together by associations, giving rise to colloidal materials,

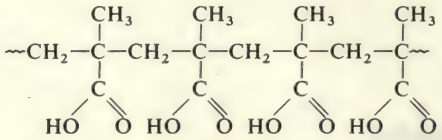


Some people feel now that it might have helped had the chemists of that day investigated early synthetic polymeric products. Instead, such were usually discarded as being oils or tars ("gooks"). To be fair to the chemists of that period, however, one should not forget that in spite of the general attitude of the time, the structure of polyethylene glycol ($n = 6$), for instance,

$$HO{-}CH_2{-}CH_2{+}O{-}CH_2CH_2{+}_nO{-}CH_2{-}CH_2{-}OH$$

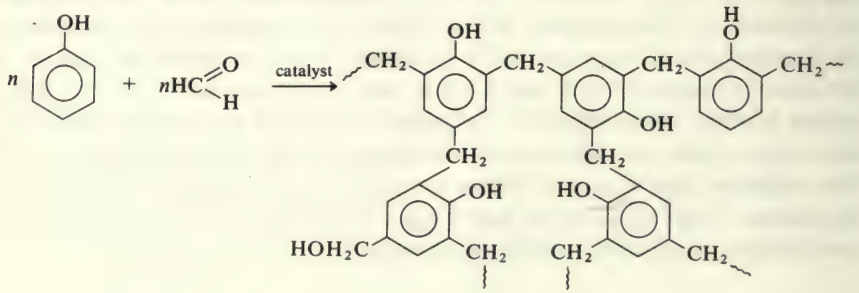
was correctly assigned in 1860 and the concept of extending the structure to very large molecular weights by continued condensation was understood (*4–6*).

At the same time, polymethacrylic acid, which we now know to be a linear molecule,



was prepared in 1880 (*7*). But, here too, unfortunately a cyclic structure was assigned which was believed to be attached to other cyclic structures by "partial valences," thereby forming gels. What is more noteworthy is that Emil Fischer and his co-workers studied many natural polymers, such as rubber, starch, polypeptides, cellulose, and lignin. His work probably entitles him to be called the spiritual father of polymer chemistry. During that period, Willstätter worked on the synthesis of polysaccharides, and studied lignin and enzymes (*8*).

One should also acknowledge the fact that in spite of ignorance of structure, many inventors developed ways to convert cellulose into its acetate ester and then used the product to make fibers, films, and coatings; they also converted cellulose into cellulose nitrate, which was used to prepare explosives and other products. At the turn of the century, Baekeland formed a hard resin by condensing phenol with formaldehyde (*9*),



The evolvement of our present-day understanding of polymeric structures occurred within the last 30–40 years.

In the early 1920s, Staudinger et al. firmly established the existence of macromolecules (*10–15*). Others, by X-ray analyses and careful use of

molecular-weight determinations, confirmed his findings (*16*). In 1929 a series of outstanding investigations were started by Carothers on polymers; this resulted in much of today's knowledge and understanding (*17*).

Now, we know that a typical molecule such as polyethylene can have a contour length of 25,000 A, but a diameter of only 4.9 A. Such a molecule can be compared in dimensions to a snarled clothesline, 75 feet long and $\frac{3}{16}$ inch in diameter. Furthermore, recent work with naturally occurring macromolecules, such as nucleic acids, for instance, revealed even more startling dimensions. When molecules of virus dinucleic acids were tritium-labeled (whose nuclear emission is less than 1 micron) and then autoradiographs prepared, these showed molecules that were about 50 microns long (*18*). Such length would signify a molecular weight of 100 million. Similar work carried out on dinucleic acids of bacteria revealed even more amazing dimensions—1 mm of length and a molecular weight of approximately 200 million.

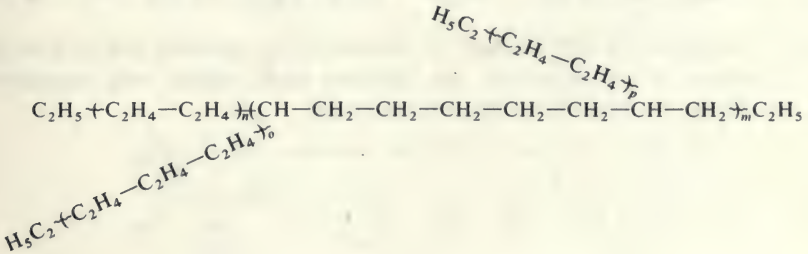
The above figures are, of course, extremes in molecular dimensions. Typical synthetic polymers will range in molecular weights anywhere from 10 to 15 thousand to several hundred thousand, although synthetic polymers in molecular weight ranges of several million are well known and actually used commercially. Interestingly enough, many of these polymers are prepared through the utilization of organic reactions that have been known for a long time. Also, new reactions and catalysts are still being discovered and applied to polymer syntheses. It is probably safe to predict that this situation will undoubtedly continue into the future.

1-2. Definitions

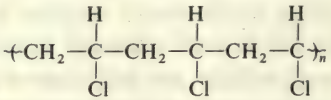
The constitution of polymers is generally described in terms of their structural units. Such units may be connected in a variety of ways. The simplest would be in a *linear polymer*, or a polymer in which the units are connected to one another in a linear sequence. A molecule of polymethylene, where units would be methylene groups, will serve as a good example,

$$H_3C\text{---}(CH_2)_x\text{---}CH_3$$

The terminal units obviously must be different from the structural units to satisfy the valence requirements. x is the *degree of polymerization*, or DP. An alternative to a linear polymer would be a nonlinear one, or a *branched structure*. As a good example of such a polymer one can think of low-density polyethylene,



Here again the terminal units are shown as being different from the rest of the constituents. It must be clearly understood, however, that there is no intent here to show them as being necessarily composed of C_2H_5 units, for other units may terminate the chains as well. This is done merely for convenience of illustration. Further propagation of branched structures would lead to *network* structures. A *planar network* would be one analogous to graphite. A *three-dimensional network* would be a *space network*, and could be compared to a diamond structure. Carothers introduced the concept of *functionality*, which states that all monomers capable of joining with only two other monomers are bifunctional (*17*). Thus he would define all the methylene units in the above structure of polymethylene as being bifunctional, and assign the functionality of *one* to the terminal methyl groups. Then x, which was defined as the degree of polymerization, also signifies the number of bifunctional units in the given linear polymer. Now, if we take as another example a linear poly(vinyl chloride) molecule of DP = 1000,

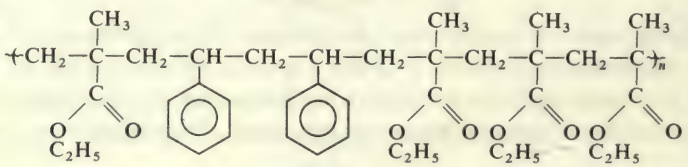


then its molecular weight should be $C_2H_3Cl \times 1000$, or (63)(1000) = 63,000.

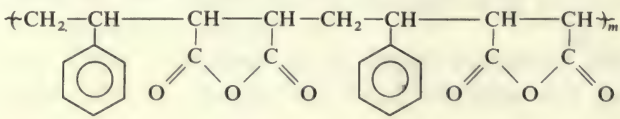
In the branched structure of low-density polyethylene shown above, the substituted ethylene units to which branches are attached can be considered to be trifunctional. The important fact to recognize here is that if the functionality of that unit were only two, branching would have been impossible.

It is also important that the *repeating unit* in the polymer must be nearly equivalent or fully equivalent to the starting material. High polymers, especially manmade, consist of molecules that in most cases vary over quite a range in their degrees of polymerization. This will be discussed in later chapters.

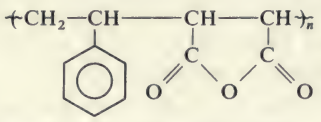
We have seen how the term "polymer" applies to substances made from either single structural repeating units or from different ones. If there are two or more structural units then the term "copolymer" is used. Such a copolymer can be linear, as for example, a copolymer of ethyl methacrylate and styrene,



Or such a structure can be branched. No regularity in repetition is shown in the above structure. When, however, the different units repeat with regularity, like a copolymer of styrene and maleic anhydride,

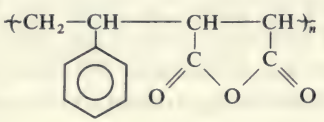


then they are regarded as alternating copolymers. Here the repeating unit is



All told, four different types of copolymer structures can be shown:

1. *Ordered-sequence copolymers* (*as above*),

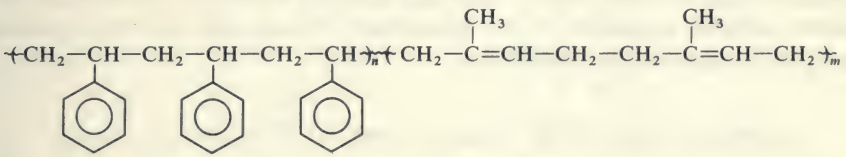


or

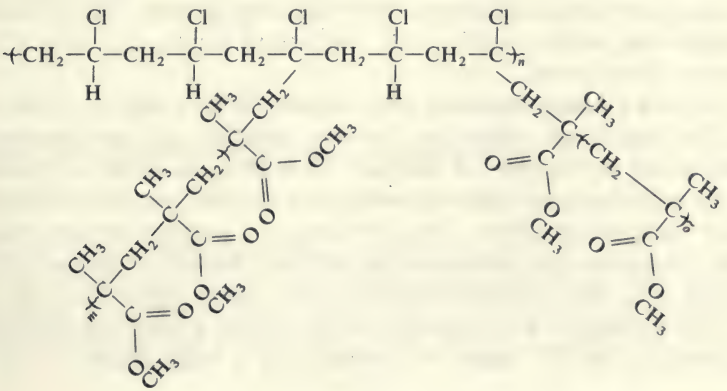
2. *Random-sequence copolymers*, as was already shown, in the case of a copolymer of styrene and ethyl methacrylate, where monomers fitted into the overall structure in a random fashion.

Both these copolymers, (1) and (2), might be identical in many aspects, such as in their average molecular weights and even in chemical compositions of the monomers from which they are put together. Nevertheless, the differences in their sequences should manifest themselves in differences in physical properties in one manner or another.

3. *Block copolymers* are copolymers made up of blocks of individual monomers. Such a copolymer would be a block copolymer of styrene and isoprene:

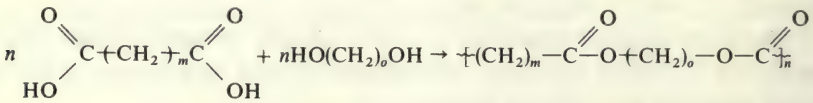


4. *Graft copolymers* are copolymers made up of backbone polymers of one type and branches of polymers of another type,

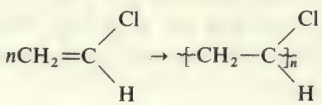


In both graft and block copolymers the length of the uninterrupted sequences can be varied to yield an entire spectra of copolymer structures. If a polymer is composed of three different monomers, it then should be referred to as a terpolymer; if composed of four as a tetrapolymer; and so on.

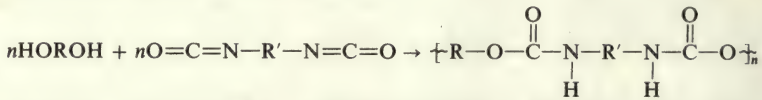
In his work on macromolecules, Carothers defined *condensation polymers* as those macromolecules in which the molecular formula or the structural units lacked certain atoms from the monomer units from which they were formed or to which they may be degraded by chemical means. He also defined *addition polymers* as those polymers in which the molecular formulas of structural units are identical with the monomer units from which they are derived (*17*). Thus, according to his definition, an example of a condensation polymer might be a polyester prepared by condensing a dicarboxylic acid and a glycol,



and an example of an addition polymer, a poly(vinyl chloride),



Since the time Carothers introduced the distinction, however, a number of polymerization processes were found that formally resemble condensation but proceed without evolution of any byproduct. An example of such a process would be formation of polyurethanes,

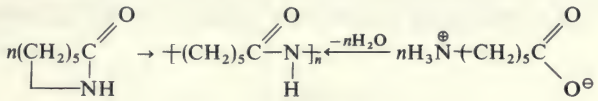


So it became common to define condensation polymers as products from reactions between pairs of functional groups that result in formation of large molecules, possessing such intermittent functional groups. The elimination of small molecules, such as water, or an acid, or an amine, etc., may or may not accompany the reaction.

It was Flory (*3*) who suggested what appears to be a superior definition. He argues that significant differences between addition and condensation polymerizations are not matters of similarity or differences in the compositions of monomer and structural units, but rather a matter of types of reaction kinetics by which the polymers form. Thus condensation polymerizations proceed by stepwise intermolecular condensations whereby addition polymerizations are associated with chain mechanisms involving active centers on the growing chains. The differences will be clearly seen from later discussions of mechanisms of polymerizations. To make the explanation a little clearer at this point,

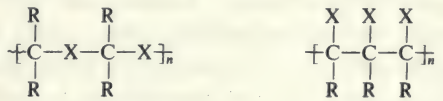
however, it may suffice to add that in addition polymerizations the chains grow by propagating the reactive sites through inclusion of monomers at such sites. Such propagations are very rapid, and chain growth takes place in a fraction of a second as chains successively add many monomer species. Thus addition-polymerization reactions usually involve merely scissions of bonds in monomers and reformations or similar connections with other monomers.

The above statement gets us into difficulty when we consider such reactions as, for instance, the conversion of caprolactam to nylon 6. This reaction can be classified as being either an addition or a condensation polymerization. Furthermore, as Stille (*19*) points out, this polymer can be made from either caprolactam or from ε-amino caproic acid by loss of water,



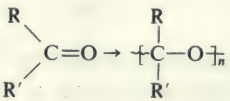
So even with the aid of a more up-to-date definition, we are still faced with the problem of having to decide whether to call this polymer an addition or a condensation polymer.

Stille (*19*) points out one other difference between condensation and addition polymers, which actually further helps in understanding the two terms. He shows that the structural units of a condensation polymer are usually joined by internal functional groups, whereas those of addition polymers usually have all-carbon-chain backbones,

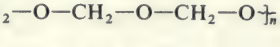


Condensation *Addition*

But, here too, obvious exceptions to all-carbon-chain-backbone addition polymers exist. These are products from polymerization of monomers in which the polymerizable double bond is not a C=C bond but a C=O bond, as in polymers of ketones,



This is also true of aldehyde polymers, or acetal resins,



We can refer to all such polymers as *condensation polymers* if we wish, but it might be more convenient to call all such polymers *addition polymers* instead.

If we wish to use generalities, we can point to the fact that today we know that the permutations and combinations that various organic structures are

capable of assuming in forming addition polymers alone are virtually infinite. Also, many of these structures might even be arrived at by alternative methods of syntheses, not even all necessarily by addition polymerizations. For instance, polymethylene may be formed from azomethane (*20*),

1. $n CH_2N_2 \rightarrow +CH_2-CH_2-CH_2-CH_2+_m$

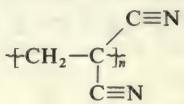
but then an identical molecule may be formed from ethylene,

2. $n CH_2=CH_2 \rightarrow +CH_2-CH_2-CH_2-CH_2+_m$

These materials were arrived at in case (1) by condensation polymerization of azomethane and in case (2) by addition polymerization of ethylene. In addition, even an all-carbon backbone can allow many different groups to be attached to it. So, by writing a model structure for many addition polymers as

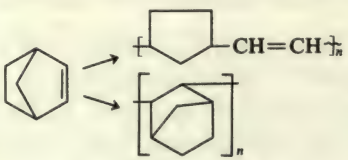
we can cover a long list of homopolymers that can be, and in all likelihood already may have been, synthesized. In this model R is more often a carbon, but might be an oxygen or even a nitrogen. R′, R″, R‴, and R⁗ can be any one of the substituents found in organic molecules. If R is an oxygen, of course, then valence considerations will make R‴ and R⁗ nonexistent. Otherwise, the four substituents can be protons, halogens, nitrides, aliphatic or aromatic groups, ketones, aldehydes, carboxylic acids or their esters, or amides. This lengthy list does not exhaust all the possibilities, because one can also include many other functional groups, such as isocyanates, nitro, azide, sulfonyl, sulfoxide, pyridine, or pyrrolidine groups. This seemingly long and all-inclusive list actually mentions only a fraction of various addition homopolymers and their copolymers, the syntheses of which were reported by various investigators.

When the starting monomer is a viscinally substituted difunctional olefin, then the product has a polyvinylidine structure as in poly(vinylidine cyanide),

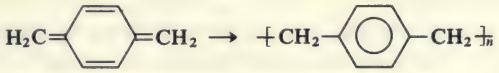


One can also polymerize many gem-disubstituted and even fully substituted olefins, whether these substituents are similar or different.

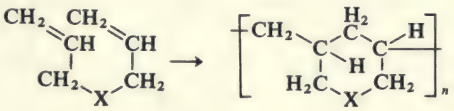
In addition, it is also possible to have polymers with cyclic structures in the backbone, such as one obtains from polymerizing norbornene to yield polynorbornene (*21*),



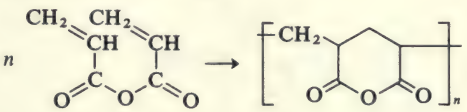
or *p*-xylylene to yield poly(*p*-xylylene) (*22–24*),



or unconjugated dienes to yield polymers with ring structures in the backbone (*25–27*),



Such rings can be prepared to possess special reactivities, as in poly(acrylic anhydride) (*28*),



By comparison, condensation polymers also offer an almost infinite variety of structure possibilities. Among the linear condensation polymers the limitations would only be in the type of condensation reactions possible. Theoretically, at least, these must be capable of proceeding indefinitely. Thus the monomer or monomers should possess two functional groups capable of entering into these reactions. But all organic condensation reactions should potentially be useful. As a result, many have been employed in such polymer preparations. Of course, steric considerations apply just as much to reactions of polyfunctional molecules as they would to monofunctional ones. When the functionality of the monomers exceeds two, then three-dimensional polymers result.

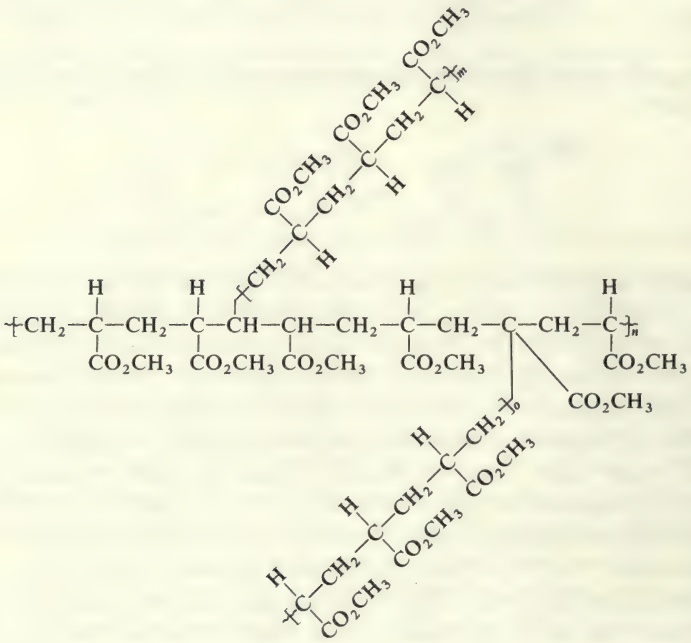
In a three-dimensional type of polymerization, after the reaction has progressed to a certain point, gelation occurs. This is a *well-defined stage* in the course of polymerization, often referred to as the *gel point*, in which transformation occurs; the reaction medium goes from a viscous liquid to an elastic gel. Prior to gelation all the polymer is soluble and fusible, but not afterward. These characteristics are attributed to restraining effects of three-dimensional or space-network structures. This leads us to a concept of dividing all polymers into two classes: (1) *thermosetting* and (2) *thermoplastic*.

To the first category belong all polymers that eventually reach gelation, or attain a cross-linked three-dimensional lattice. Raising their temperature will no longer attain plasticity, because the molecules are now interconnected and can no longer be made to flow past each other. They are thermally set and for the same reason can no longer be soluble in any solvents.

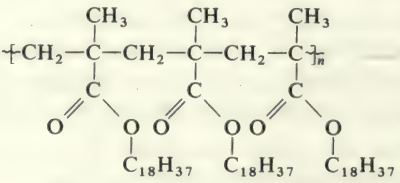
The thermoplastic polymers of the second category never attain gelation, will not cross-link, and are permanently capable of flowing upon reheating. Here the chains are not connected by cross-links and can, therefore, be separated

and dissolved in suitable solvents. For some polymers, however, suitable solvents are hard to find.

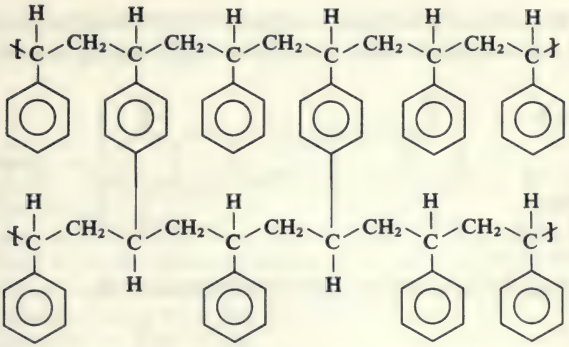
When considering branching in a polymer it must be borne in mind that the term refers only to discrete macromolecules, composed of repeat units and attached to the main polymer backbone. Long side groups inherent in the monomer itself are not considered as branches. Thus below is shown a branched polymer of methyl acrylate,



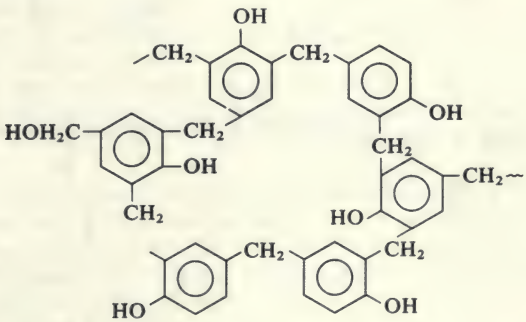
and a linear polymer of stearyl methacrylate,



An example of a network addition polymer can be a copolymer of styrene and divinyl styrene,



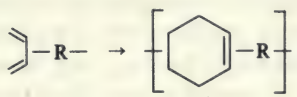
An example of a condensation network polymer is the reaction product of phenol and formaldehyde,



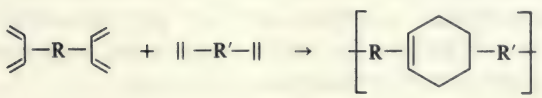
Stille (*19*) brings out an interesting point about some polymers which are prepared by reactions commonly associated with addition polymerizations, such as by free-radical mechanism, but which are actually condensation polymers. He cites condensation of nonconjugated diolefins with dithiols as an example,

$$HSRSH + CH_2{=}CH{-}R'{-}CH{=}CH_2 \rightarrow +S{-}R{-}S{-}CH_2{-}CH_2{-}R'{-}CH_2CH_2{+}_n$$

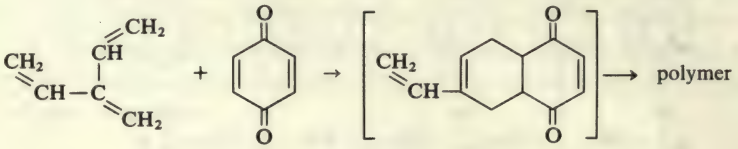
and as an opposite type, the formation of Diels-Alder polymers that should form by stepwise addition. Yet these polymers lack the characteristic condensation structure but cannot be formed by a different method:



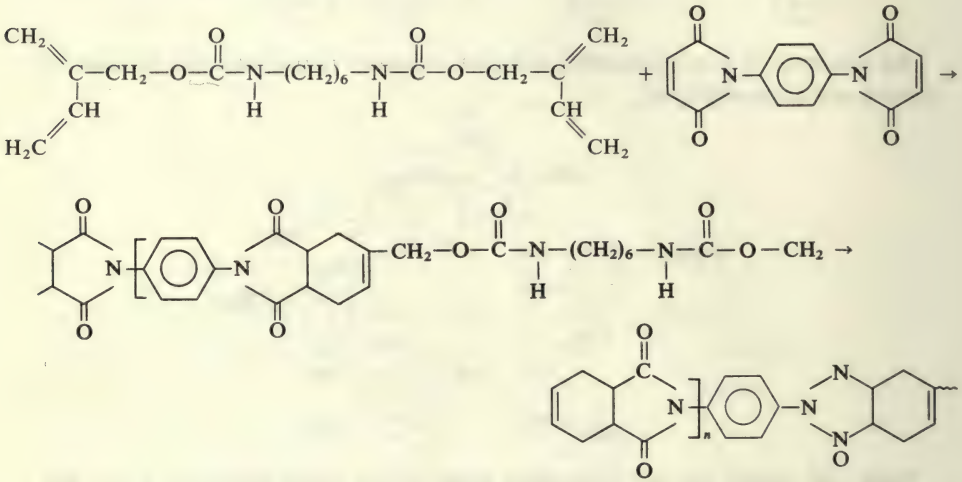
or



Another interesting example of this reaction can be found in the work of Bailey and co-workers (*29*), who reacted 2-vinylbutadiene with benzoquinone,



and hexamethylene dicarbonate with *p*-phenylenebismaleinide,



1-3. Nomenclature

The *Chemical Abstracts* recommended nomenclature for polymers is followed in many examples of chemical literature. Thus homopolymers are described by attachment of the term *poly* in front of the monomer name, as in polystyrene, polyethylene, and polybutadiene. For monomers with names composed of two words, such as methyl methacrylate or vinyl acetate, parentheses are used to indicate that poly applies to the whole term, as in poly(methyl methacrylate) and poly(vinyl acetate). By this system of nomenclature, random copolymers may be designated by the prefix *co*, as in poly(butadiene-costyrene) and poly (vinyl chloride–covinyl acetate). Alternating copolymers can be differentiated by substituting *alt* for *co*, as in poly(ethylene–*alt*-carbon monoxide).

To describe graft copolymers, the prefix *g* may be used, and for block copolymers, *b*. In such a system of nomenclature, the first polymer segment named corresponds to the homopolymer or copolymer formed in the first stage of synthesis. In a graft copolymer this will represent the backbone. An example of this will be poly(ethylene–*g*-acrylonitrile) or poly(butadiene–costyrene–*g*-styrene-cobutadiene). Similarly, for block copolymers, poly(styrene–*b*-methyl methacrylate) or poly(methyl methacrylate–*b*-styrene).

Conventional prefixes indicating *cis* and *trans* isomerism are inserted in front of the polymer name, as in *cis*-1,4-polyisoprene, or *trans*-1,4-polybutadiene.

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Physical Properties of Macromolecules

2

When an organic chemist is concerned with physical properties of organic compounds, he may wonder how they are influenced by molecular sizes, the nature of primary and secondary bond forces, molecular symmetry or dissymetry, and arrangements and configurations of molecules into either amorphous or crystalline materials. His interests may often be motivated by the fact that these properties affect melting points, solubilities, melt and solution viscosities, tensile strength, etc. Molecular sizes and the means for their determinations will be considered in Chapter 3. Here we shall consider the remainder of the above properties.

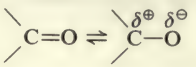
2-1. Secondary Bond Forces

In an organic macromolecule, the bonds holding the molecule together will usually be covalent and in no way different from those holding small molecules together. But, whereas the secondary bond forces play only a relatively minor part in influencing the properties of small molecules, in polymers these assume an important role. Generally speaking, it is well established that in most covalent molecules, large or small, even after all primary valences are satisfied, there still remain intermolecular forces acting between molecules. These forces are van der Waals' forces and hydrogen bonding.

The first can be divided into three types:

1. *Dipole-dipole interactions.* These are interactions by molecules carrying equal and opposite electrical charges. The magnitude of these interactions depends upon the alignment of the dipoles with one another. And, because molecular orientations of this sort are always opposed by thermal agitations, the dipole forces are strongly temperature-dependent. Ingold (*1*) points out that almost all molecules will possess a number of electrostatic characteristics. These can be summarized in terms of general terminology as polarization. What this implies is that molecules possess external electrostatic fields. Such fields when produced by ionic species, are long range. Medium-range fields can also

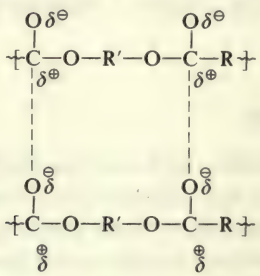
be produced but by molecules that have no net charges but have dipole moments. The potentials of such medium-range fields will be proportional to dipole moments and will vary inversely in field strength with squares of the distances. They will also depend upon direction, the positive ends of these fields being near the atoms that are commonly electropositive, but the electronegative ends are near the atoms that are more electronegative in nature,



When an electrostatic charge or number of charges are placed within the effective range of any of these fields, they will be subjected to a force. This force will be proportional to the gradient of the potential, and the force acting on a dipole will be proportional to the spatial rate of change of the gradient, etc.

Ingold also points out (*1*) that whereas the most important, and longest range, forces are those between ions, the next would be the ion dipole forces, and after them dipole-dipole interactions.

An example of such a dipole-dipole interaction would be secondary bond forces occurring between two chains of linear polyesters. Each C=O bond of the polyester would set up a field through polarization. This field would tend to interact with another field of a similar nature on the other chain,



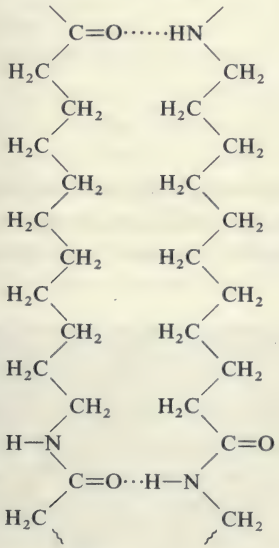
As a result, cohesion exists between the chains.

2. *Induction forces.* When a covalent molecule is placed in an electrostatic field, one associated with a dipole coming from another molecule, a slight displacement of the electrons and nuclei can result in the original molecule. This is a case of an *induced dipole.* The intermolecular force with which the two dipoles, permanent and induced, will attract each other is called the *induction force.* The energy of the induction force is always small and is not temperature-dependent.

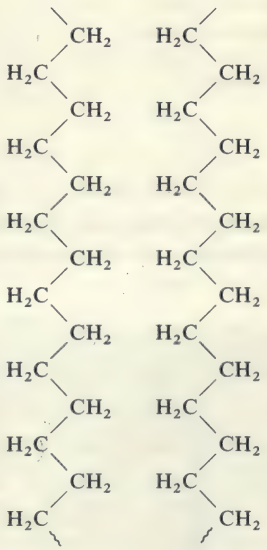
Streitweiser comments (*2*) that the electrostatic interaction between two neighboring dipoles oriented in similar directions results in lessening of charge displacement and consequent decrease in dipole moment. In effect, the polarization induced by neighboring dipoles changes the ionic character, or the hybridization of a bond, or both.

3. The third force would arise from a different type of polarization of molecules, which is not caused by a permanent dipole of a neighbor. Rather, time-varying dipoles of molecules, which average out to zero, come into play. These arise from different instantaneous configurations of the electrons and nuclei about the bonds of the chain.

The overall bond energy of all the secondary bond forces combined range between 2 and 10 kcal/mole. Of these, the hydrogen bond, which we shall regard here also as a secondary bond force, takes the greatest share of the bond strength. Table 2-1 shows the magnitude of the intramolecular forces in many macromolecules. Of these, the strongest and most influential is the hydrogen bond. For example, one need only compare the physical properties of, say, nylon 11, with those of linear polyethylene. The structures of the two molecules can be represented as follows:



nylon 11



polyethylene

One can see that structurally they are quite similar, with the exception of the amide link in Nylon 11. Yet comparison of physical properties shows the magnitude hydrogen bonding plays in affecting differences. Nylon 11 melts at 184–187°C and will dissolve only in very strong solvents, such as formic or sulfuric acid. Polyethylene (linear), on the other hand, melts at about 130°C or slightly higher and is soluble in hot aromatic solvents.

Miscibility and solubility are, of course, determined by intermolecular forces. In addition, if these are small and the cohesive energy low (1 to 2 kcal per mole), then the polymers will have relatively flexible chains that will respond readily to applied stresses and will have properties of elastomers. But, when the cohesive energy is high (above 5 kcal per mole), the material will have high

TABLE 2-1
Molecular Cohesion in Linear Polymers[a]

	Cohesion per 5 A chain length, kcal/mole	Cohesive energy density, cal/cm^2
Polyethylene	1.0	62
Polybutadiene	1.1	—
Polyisobutylene	1.2	65
Rubber	1.3	67
Poly(vinyl chloride)	2.6	91
Poly(vinyl acetate)	3.2	88
Polystyrene	4.0	74
Poly(vinyl alcohol)	4.2	—
Polyamides	5.8	185 (nylon 6-6)
Cellulose	6.2	—
Polyacrylonitrile	—	237

[a] From Reference *3*.

strength, will exhibit resistance to applied stresses, and will usually possess good mechanical properties. Should the molecule in addition possess symmetry, there will also be an accompanying strong tendency to form ordered crystalline regions.

2-2. Crystallinity

Crystallinity in polymers is somewhat different in nature from that of small molecules. Small molecules can be either totally amorphous (which is true if they are impure) or totally crystalline at proper temperature. The polymers, on the other hand, are divided into two categories: those which are completely amorphous under all conditions, and those which are partly crystalline. Polymers that are partly crystalline can, of course, also be amorphous under certain conditions, as when they are above their melting temperatures, etc.

X-ray diffraction studies are often employed in determining crystallinity in polymers. The diagrams show a series of sharp rings that come from crystalline regions. These sharp rings will be superimposed over diffuse scatterings which arise from amorphous regions. This is due to the fact that in a partly crystalline polymer we have a crystalline order called *crystallites* which is surrounded by an amorphous matrix. These individual crystallites are small, usually averaging 100 A × 200 A × 200 A in size. In addition, these small crystallites tend to aggregate into larger regions called *spherulites*, which often become large enough to be seen with a polarizing microscope. Because the length of each individual polymer molecule is often such that a single crystallite is much too small for the whole molecule to fit into it, we find that the same chain will

traverse a crystallite, then pass through an amorphous region from which it will again enter another crystallite, and so on.

The larger spherulite may be recognized by appearing to resemble a Maltese extinction cross when viewed with a polarizing microscope. Their study reveals spherically symmetrical organizations of birefringent units. When investigated in greater detail, the spherulites are found to possess characteristic morphology formed by radiating, fanning growths of fibrous units leading at first to sheaves and then to spherulites. The molecules are apparently always perpendicular, or nearly perpendicular, to the spherulite radius. It is now generally agreed (*4b*) that spherulitic crystallization is typical of crystallization in bulk (Figure 2-1).

In many cases one can also observe periodic extinction patterns, usually in the form of concentric rings in the spherulites. The presence of these rings has been attributed to twisted arrangements of the crystalline units along the spherulitic radius. This interpretation, although first disputed, now appears to have received general recognition (*5*). By using the observed extinction patterns, a variety of different twists are being deduced for many polymers.

The word *crystallite* really means that certain volume elements of a polymeric system have attained a state of three-dimensional order. This order resembles the orderly arrangement of small molecules in crystals such as those of benzene or sucrose. The shape of crystalline domains of polymeric materials differs, however, from shapes of normal crystals in that these are much smaller in size, possess many more imperfections, and are connected by disordered, amorphous areas of through-going polymer chains. As a result, no sharp boundaries exist

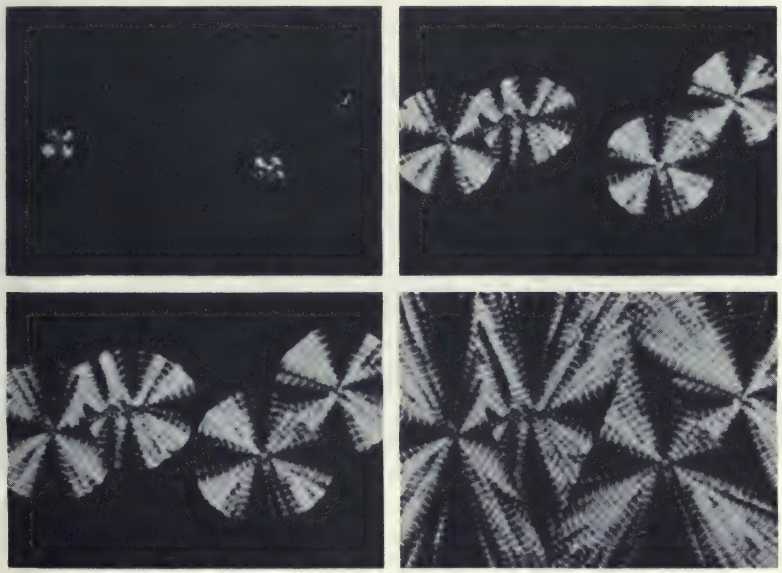


Figure 2-1. Spherulite growth formed from a melt. (From Reference *21*; courtesy of the *Journal of Polymer Science*.)

between laterally ordered (crystalline phase) and disordered (amorphous phase) parts of the system.

A very interesting electron micrograph was made recently by Keith et al. (*4a*) of polyethylene showing links between crystals. This was accomplished by crystallizing the material from a melt after it was blended with a hydrocarbon, n-$C_{32}H_{66}$. After crystallization took place, the hydrocarbon was washed away with a solvent, exposing the polymer crystals and showing the links joining them together (Figure 2-2).

Hammer and Geil (*6*) proposed a hypothesis for the mechanism of nucleation. It is based on the idea that in a mass of molten polymer, 20–30°C above the melting point, segmental motion is rapid, jumps occurring more often than 10^6 per second. These jumps produce small order within small regions for very short intervals. At some temperature the critical crystallite size will be the same as that of ordered regions produced by the segmented jumps. At this point, nucleation begins and a stable crystallite forms and grows.

The crystallite can grow in two ways: by alignment of additional molecule segments already in the nucleus, and by addition of new molecule segments. While the first crystallite grows, other nearby regions, subcritical in size, will become stable and also grow (nucleate). According to this hypothesis, spherulite growth results in growing crystallites inducing nucleation in their vicinity.

Besides growing crystals from a melt, it is also possible to grow single crystals from dilute solutions (*7–9*). The first observations were made on polyethylene, but these were followed by growing other polymeric crystals, such as polyoxymethylene (*10*), polyamides (*11*), poly(4-methylpentene-1) (*12, 13*), polypropylene (*14*), polyoxyethylene (*4b*), and cellulose (*15*) (Figures 2-3 and 2-4).

The basic units in single crystals are lamellae about 100 A thick. Electron-diffraction studies reveal that the molecules are arranged perpendicular, or nearly so, to the layers, which are much thinner than the overall lengths of the molecules. This can only mean that the molecules are somehow folded into these crystals. Such regular, sharp, folded configurations were postulated by Keller (*8*). He suggested that the fold length corresponds to the layer thickness. The detailed structure of the fold is still unknown. Many types appear to occur within the same crystal (*16*). Furthermore, the fold length seems to vary with the crystallization temperature (*17*). In the case of polyethylene there is also conclusive evidence that the chains fold or pleat in a very regular manner.

Wunderlich (*18*) commented that even though a perfectly crystalline polymer has not been obtained in the laboratory, several linear polymers have now been grown in a highly crystalline form (*19–20*). In solution, the randomly coiled chains are widely separated and disentanglement is facilitated. So the crystals resulting from solution crystallization appear quite perfect. But because the chain direction is 100 A in the thin lamellae and the chain length is 20,000 to 30,000 A, chains must fold at top and bottom. Also, because of their high surface-free energy, the folded chain crystals are metastable. This apparently leads to surface defects.

Figure 2-2. Electron micrograph of polyethylene, showing links joining the crystals. (From Reference *4a*; reproduced with permission of Bell Laboratories.)

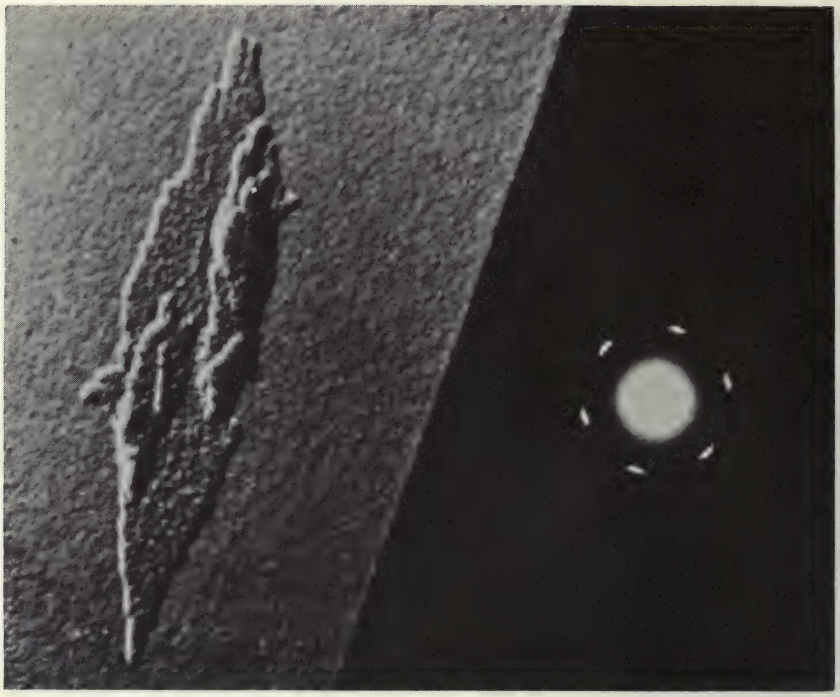


Figure 2-3. Single crystal of polyacrylonite and its electron-diffraction pattern. (From Reference *21*; courtesy of the *Journal of Polymer Science*.)

Our present-day understanding of the folded-chain model of crystal growth from dilute solution was summarized by Peterlin (*21*). Originally it was postulated that a single polymer chain was included in one single crystal. X-ray diffraction patterns, however, demonstrated that amorphous regions are present. This and density defects were attributed to crystal defects, particularly to chain folding at crystal surfaces. As a result, the postulate was modified by recognizing that what is happening is that some chains become folded back in a switchboard manner. Such folded chains are now believed to be quite similar to the tied molecules within amorphous regions of polymers crystallized from melt, where single chains become incorporated into more than one crystal.

2-3. Steric Configurations of Polymers

One can look upon the linear polymerization process in general terms as a process creating an order in one dimension out of a random collection of small molecules. Once these molecules are combined to form chains, the neighbors are then joined to stay together through all subsequential transformations. But any disorder that might have been introduced during the process of

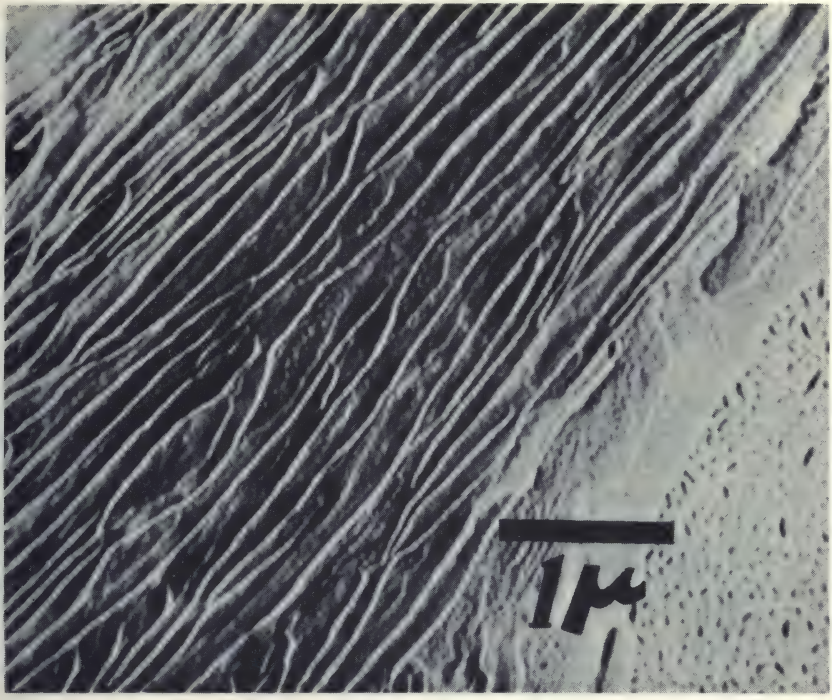
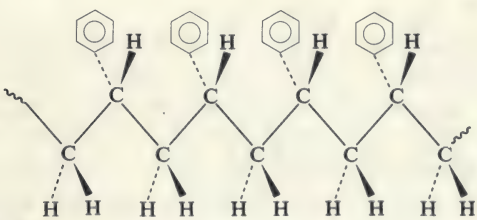


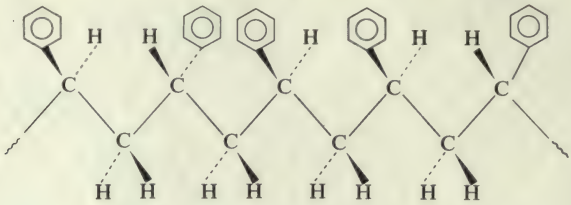
Figure 2-4. Lamellae of polyethelene crystallized from the melt in the form of a thin film. (From Reference *21*; courtesy of the *Journal of Polymer Science*.)

polymerization will later interfere with the process of three-dimensional crystallization. Such a disorder might have occurred by a variety of mechanisms involved in the assemblage of the monomeric units. Or a disorder can be the result of the assemblage of different kinds of monomer, or it can even be the result of random-chain distributions. Now, as already stated, the polymeric chain's ability to pack into orderly crystalline array is a function of the regularity of the chain. Styrene, for example, can be synthesized in two forms, *isotactic* and *atactic*. In the first case, the phenyl groups are all arranged on the same side of the chain, either all up or all down. By picturing the chain backbone as drawn in the plane of the paper and picturing all phenyl groups so oriented as to be above the plane, one can show isotactic polystyrene,



isotactic polystyrene

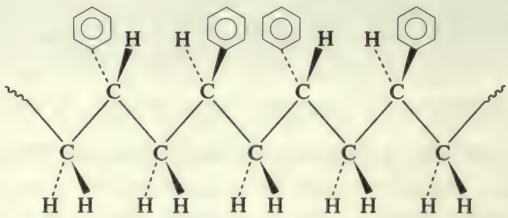
But in an atactic (or heterotactic) polystyrene the phenyl groups are completely at random, both up and down, or behind the plane of the paper,



atactic polystyrene

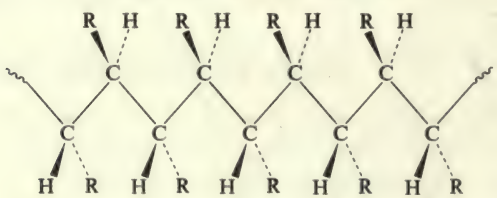
This difference in arrangement shows up in physical properties. The isotactic isomer is crystalline, melts at 250°C, and is insoluble in most common solvents. The atactic variety, on the other hand, is amorphous, low-melting, and readily soluble in most solvents.

Natta (*22, 23*), who deserves the credit for initiating this system of nomenclature for stereospecific macromolecules, also introduced a third term, *syndiotactic*, to designate polymers possessing alternating orientations for the adjacent centers,



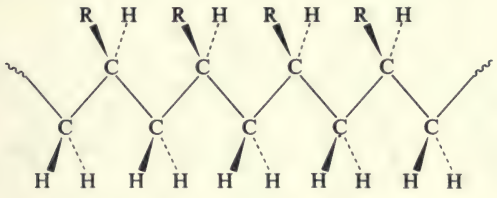
syndiotactic polystyrene

Since the introduction of the three terms, the evolving ability to regulate steric arrangement of macromolecules necessitated a system for naming high polymers possessing various types of steric regularity. The International Union of Pure and Applied Chemistry has recommended the nomenclature suggested by Huggins et al. (*24*). Thus they would picture isotactic polyethylidine, called isotactic poly(methyl) methamer, or *it*$[CH(CH_3)]_n$ as



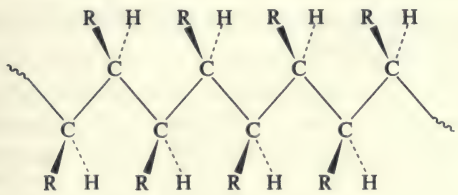
Fischer projection

isotactic polypropylene or isotactic poly(methyl) ethamer, $it[CH_2CH(CH_3)]_n$, as



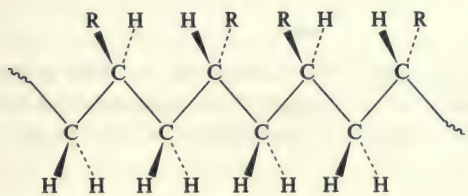
Fischer projection

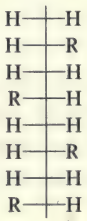
a syndiotactic polyethylidene or a syndiotactic poly(methyl) methamer, $st[CH(CH_3)]_n$, as



Fischer projection

and a syndiotactic polypropylene or sydiotactic poly(methyl) ethamer, $st[CH_2CH(CH_3)]_n$, as

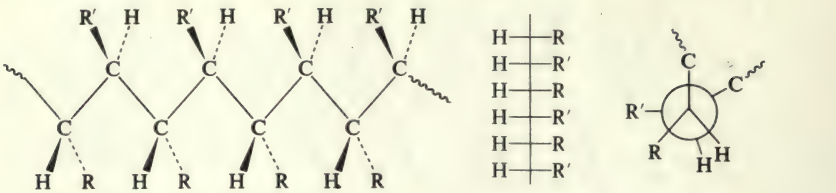




Fischer projection

When two adjacent carbons in a polymer are substituted, a diisotactic arrangement is possible. Here a threo-erythro terminology was needed. Thus an erythrodiisotactic polymer would be one composed of alternating substituents -(-CHR—CHR'-)-_n, with all R groups to one side of the chain and the R' to the opposite side. This can probably be more easily visualized by using both the Fischer and the Newman projections. So a molecule of erythrodiisotactic poly(2-pentene), or erythrodiisotactic poly(1-ethyl) (2-methyl) ethamer, would

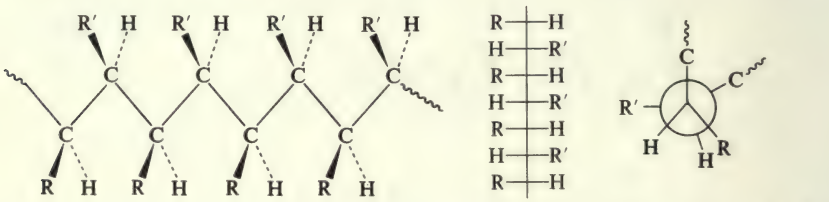
be *eit*$[CH(CH_3)CH(C_2H_5)]_n$, and can be shown as



Fischer projections *Newman projection*

erythrodiisotactic polymer

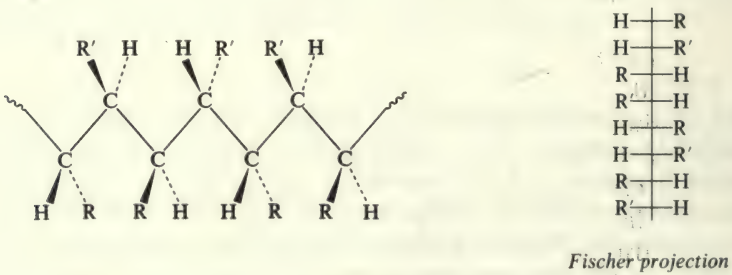
and the threodiisotactic polymers would be the threo isomers. Thus a threodiisotactic poly-2-pentene or threodiisotactic poly(1-ethyl)(2-methyl) ethamer, *tit*$[CH(CH_3)CH(C_2H_5)]_n$, can be shown as



Fischer projection *Newman projection*

threodiisotactic polymer

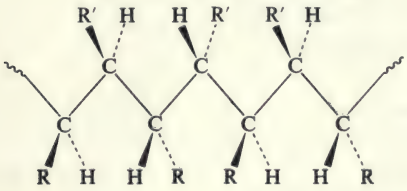
In the same way, both erythro and threo isomers are possible of the syndiotactic polymers. An erythrodisyndiotactic poly(2-pentene) or erythrodisyndiotactic poly(1-ethyl)(2-methyl) ethamer, *est*$[CH(CH_3)CH(C_2H_5)]_n$, can be represented in this manner:



Fischer projection

erythrodisyndiotactic polymer

and threodisyndiotactic poly(2-pentene) or threodisyndiotactic poly(1-ethyl) (2-methyl) ethamer, *tst*$[CH(CH_3)CH(C_2H_5)]_n$, can be represented as



treodisyndiotactic polymer

Fischer projection

There is little doubt that the tendency to crystallize plays a very important part in the thermal and mechanical behavior of macromolecules. The main contributing factors to the tendency to establish this three-dimensional order were summarized by Mark (*25*):

1. Structural regularity of chains, which leads to establishment of identity periods.
2. Free rotational and vibrational motions in the chains allowing different conformation to be assumed.
3. Presence of groups capable of producing lateral intermolecular bonds (van der Waals' forces) and regular, periodic arrangement of such bonds.
4. Absence of bulky substituents, spaced irregularly, which would prevent segments of the chain from fitting into a crystal lattice as well as prevent laterally bonding groups from approaching each other to a distance of best interaction.

The differences in properties of the macromolecules which result from these various steric arrangements are quite substantial. The atactic polymers are very often amorphous and noncrystalline. They also usually have low softening temperatures. Completely isotactic or syndiotactic polymers, on the other hand, are generally found to be much higher melting, more often crystalline, and have better mechanical properties. In addition, differences from the nature of the R group are significant. Thus there is a progressive rise in melting points in vinyl polymers, $+CH_2—CHR+_n$, with the bulkiness of the R groups. The structure of these polymers is such that considerable rotation is required (judging from molecular models) to avoid overlap of the R groups. If this rotation is carried out uniformly in one direction, the molecule is wound into a helix. Natta and coworkers (*26*) actually found that this is exactly what happens in the hydrocarbon polymers. The important thing is that the helical form evidently does not arise during crystallization but is a property of the individual molecule imposed by steric factors. Molecular-model studies reveal that a helical model is quite stiff and essentially a somewhat bulky rod.

2-4. First-Order Transition Temperature

It should be possible to summarize the subject of crystallization by saying that crystalline polymers are characterized by the following:

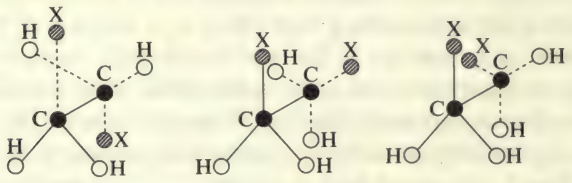
1. Arrangement of the atoms in the unit cells.
2. Fraction of crystalline material present.
3. The size of the crystallites.
4. The shape of the crystallites.
5. Orientation of the crystallites.
6. Aggregation of the crystallites.
7. Melting temperature of the crystallites, T_m.

Of these, the first six are primarily of interest to the physicist and physical chemist. The last one, however, concerns the organic chemist as well.

The melting temperature of the crystallites, T_m, is often designated as the first-order transition temperature. These are not as sharp as melting points of true crystals, for they usually melt over a range. Some typical T_m's are shown in Table 2-2.

In addition to possessing or lacking certain symmetrical arrangements within their chain compositions, linear high polymers must assume certain stable conformations for aligning themselves into crystalline regions. Beyond that, even in amorphous regions, there may be inherent tendencies for the chains to assume preferred conformations.

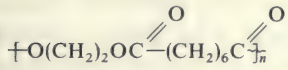
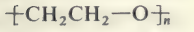
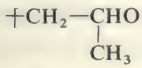
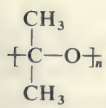
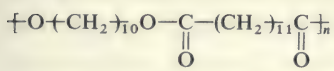
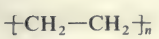
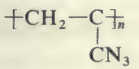
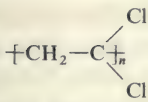
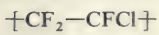
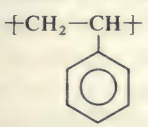
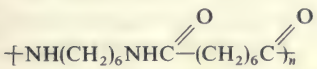
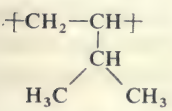
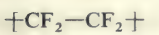
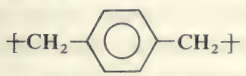
Mizushima and Shimanouchi (*27*) studied internal rotations of molecules. They demonstrated that in simple molecules the *trans* and *gauche* forms were the preferred configurations,



trans form *gauche form*

Judging from that, they expressed the opinion that it is very probable that among linear high polymers which possess only single bonds the unit structures will also be either *trans* or *gauche*. For molecules possessing carbonyl groups, or hydrogen bonds or forming coordination bonds, the two forms will also be stable. The case of the carbonyl group, however, should be special in that the internal rotation angles would be somewhat different from ideal. Furthermore, their experimental results indicated that van der Waals' repulsive interaction and electrostatic interaction between the movable groups are responsible for creating hindering forces.

TABLE 2-2
T_m of Some Polymers[a]

Repeating units	Appr. m. p., °C
	45
	66
	70
	58–60
	80
	130
	160
	210
	210
	230–240
	235
	300
	327
	380

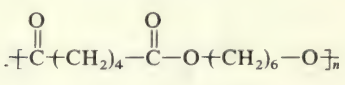
[a] From Reference *25* and various other sources.

2-5. Effect of Chemical Composition on Properties

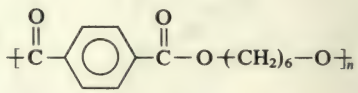
The term *flexibility* in linear macromolecules implies activation energies necessary to initiate vibrational and rotational motions around single bonds. As a result of such motions, chains are capable of assuming various conformations at relatively moderate temperatures and within short periods of time. The energy barriers separating various specific individual conformations in small organic molecules had received thorough scrutiny from various investigators, who studied specific heats, infrared absorption, and magnetic resonance. This led to a good understanding of the stability of various conformational isomers, as well as the rates at which equilibrium between them was established. This information has been applied to macromolecules. The following conclusions were reached (*25*):

1. Linear polymers possessing only single bonds in their backbones between atoms, C—C, or C—O, or C—N, permit rapid conformational changes.
2. Ether and imine bonds or double bonds in the *cis* form tend to reduce energy barriers and thereby "soften" the chain, making the polymer less rigid, more rubbery, and easier soluble.
3. Cyclic structures in the backbones of polymer chains strongly inhibit conformational changes and make crystallization difficult.

Generally, freedom of molecular motion along the chain backbone contributes to lowering the first-order transition temperature (T_m). On the other hand, chains with bulky groups, such as polytetrafluoraethylene, have higher melting points than polyethylene. Dipole force must play a part here, too, of course. The substitution of a rigid unit into the backbone raises the melting point. Thus replacement of a methylene unit by a phenylene unit results in higher T_m. For example, poly(ethylene adipate) melts at 50°C, whereas poly(ethylene terephthalate) melts at 265°C,



poly(ethylene adipate)



poly(ethylene terephthalate)

As the number of methylene units separating polar groups or H-bonding groups in a polymer chain increases, the polymer becomes more like polyethylene and the melting points tend to approach that of polyethylene (*28*); see Figure 2-5.

It is interesting that the melting points of polyesters, as seen from Figure 2-5, should lie below polyethylene, although the polyesters contain polar groups. Probably the effects of the secondary bond forces are smaller than the effects of flexibility imparted by C—O—C groups of the esters to the chains.

In a given type of polymer, such as the polyamides, polyureas, or polyurethanes, the melting point is influenced by the number of methylene groups present, specifically whether this number is odd or even between the polar

groups. These individual types of macromolecules will be discussed in the chapters dedicated to them.

Within polyhydrocarbons the effect of pendant groups upon melting is quite interesting. All linear polyethylene, as already mentioned, melts at 130°C or higher (*29*). By increasing the size of the pendant groups in the higher isotactic poly(1-olefin) starting with polypropylene, which melts at 165°C (*23*), the lengthening of the side chain decreases the melting point until we reach polyhexene. At that point the minimum takes an upturn (*30*). This phenomenon has been attributed to side-chain crystallization (*31*).

The next series of polymers to be examined are those formed from analogs of the olefin $CH_2{=}CH{-}CH_2{-}CH_2{-}CH_3$. Any branching on the α-carbon will yield the highest-melting polymers (*31*), which will fall in the range 250–360°C. Here polystyrene and poly(3-methyl-1-butene) are good examples. Branching on the β-carbon, if symmetrical, will give melting points in the range 225–240°C (*31*). Unsymmetrical branching will result in lower melting points. Branching on the γ-carbon or further out on the chain results in lower melting points. Terminal branching results in rubbery polymers.

Copolymers have generally lower melting points than either of the homopolymers prepared from the comonomers. By increasing the amount of a comonomer the melting point is decreased until a minimum (which might be compared to a eutectic) is reached.

The tightest internal arrangement of macromolecules is achieved by crystallinity. As a result, the density of a polymer will be directly proportional to the degree of crystallinity. And, as is probably becoming clear by now, highly crystalline polymers usually possess high tensiles, are stiff and hard, and are poorly soluble in common solvents (*32*). Of course, the solubility of any polymer is a function not only of the crystallinity but also its internal structure and its molecular weight. The solubility will generally decrease with an increase in molecular weight. But the fact that crystalline polymers are less soluble than the amorphous ones can be attributed to the binding forces of the crystals, which have to be overcome to achieve dissolution. Once in solution, however, crystalline polymers cannot be expected to exhibit different properties than amorphous ones.

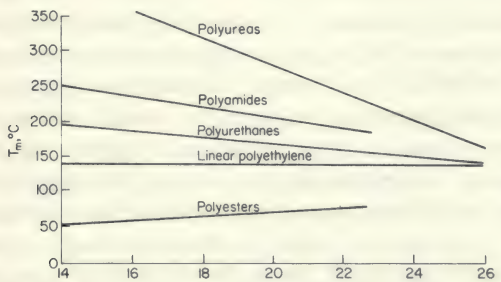


Figure 2-5. Trends in T_m for various aliphatic polymers.

In studying the effect of structure on flexibility of polymers, Greenberg and Alfrey (*33*) found that an increase in the length of pendant *n*-alkyl groups will cause a proportional increase in flexibility of the polymer. The maximum is reached when the pendant group is *n*-octyl, after which there appears to be a reversal of this trend. They suggested that this reversal can also be attributed to the increasing tendency of the side chains to crystallize.

2-6. Orientation

When a molten polymer is allowed to crystallize, the crystallites will tend to form in a random fashion in the absence of any external force. But when an external force is applied, a rearrangement of the crystalline material takes place. X-ray diagrams demonstrate that under the influence of applied stresses, the crystallites become *oriented*, in that the chains align themselves in the direction of the applied stress. This is reflected in the fact that now the polymer has the greatest strength along the line of orientation. Generally, the degree of crystallinity remains the same during drawing, provided it was well developed before it, but the arrangement of the crystallites changes. However, if the crystallinity was not developed before the drawing, and if the polymer happens to be amorphous, or only partly crystalline, then the amount of crystallinity will probably increase. The exact mechanism of this is still being investigated.

2-7. Second-Order Transition Temperature

As the temperature of polymer is being lowered, the amorphous regions will gradually harden and embrittle like glass. The transition temperature between the rubbery stage and the glassy stage is designated as T_g, or the *second-order transition temperature*. Sometimes it is also referred to as the *glass transition temperature*. In this change are manifested changes in specific volume, heat content, thermal conductivity, refractive index, dielectric loss, and, of course, stiffness.

What might interest a chemist is that above T_g there is the ability of chains to undergo cooperative localized motion. Below the glass transition there is insufficient thermal energy available to enable whole segments of the polymeric chains to move. Only individual atoms are capable of making small excursions about their equilibrium positions. The structure resists deformation and is stiff and brittle. But when sufficient heat input into the material again takes place, so that the temperature will rise above T_g, the larger molecular motion involving coordinated movement becomes possible. On a macroscopic scale the polymer above T_g is a solid, for it still has dimensional rigidity, but on a microscopic scale it now behaves, to some extent, like a liquid, for large elastic deformations are possible. As a result, the material becomes tougher and more pliable.

A few typical T_gs are listed in Table 2-3. It is important to realize that whereas not all polymers will have a T_m (only those which are partly crystalline), all polymers will possess T_gs.

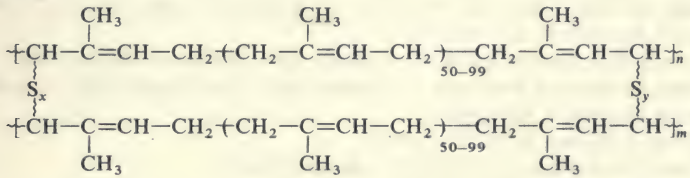
TABLE 2-3
A Few Typical T_gs[a]

	T_g, °C
Nylon 6-6	47
Poly(methyl methacrylate)	57–68
Silicone rubber	−123
Cellulose nitrate	53
Polyisobutylene	−70
Polystyrene	81
Poly(vinyl chloride)	75
Polybutadiene	−85
Natural rubber (polyisoprene)	−70
Poly(ethyl acrylate)	−22
Poly(methyl acrylate)	5
Poly(*n*-butyl methacrylate)	22
Poly(*n*-butyl acrylate)	−56
Poly(vinyl acetate)	30
Poly(vinylidine fluoride)	−39
Poly(ethyl methacrylate)	65

[a] Average approximate values taken from References *34* and *35*.

2-8. Elasticity

The phenomenon of elasticity of rubbers or elastomers is of major importance to polymer chemistry. A vulcanized rubber, whether natural or synthetic, is essentially a single giant molecule. Vulcanization or cross-linking may be considered typical when it occurs every 50th or 100th unit along the chain,



The cross-links need not necessarily be sulfur, as shown. Nor, for that matter, does every cross-link have to be on alpha carbons. What is important, however, is that the one important physical state exhibited by *cis*-polyisoprene or by other rubbers is the reversible elastic deformations of which these materials are capable. Most polymers will exhibit this to a limited extent, but this property is best developed in materials that possess just sufficient cross-linking to build up three-dimensional networks. Some of these rubbers are actually capable of deformations of several hundred per cent.

The best explanation for this phenomenon is the fact that the chains tend to form highly kinked amorphous conformations between the cross-links.

Owing to these conformations, the distance between the ends is much less than the fully outstretched lengths. Deformation (or stretching) of the rubber straightens out the molecules, which tend to return again to the kinked state when the deformation state is removed. Thus each molecule behaves like a spring and the overall elastic modulus of rubber is determined by the number of springs, i.e., of cross-links, in the rubber.

2-9. Optical Activity in Polymers

In polymers the optical activity depends mainly upon groups located immediately near the asymmetric carbon atom. As structural dissymmetry is removed from the asymmetric center, the activity decreases rather rapidly, dropping to a negligible value. In a homopolymer structure differences of the two chains attached to the center of asymmetry would be found in the nature of end groups, the relative lengths of each chain as well as the configurations of the two substituted carbon atoms on adjacent monomers. The amount of optical activity that may be expected to be caused by these entities would be insignificant, because the environment surrounding the asymmetric carbon is quite similar.

Gross dissimilarities in the immediate vicinity of the asymmetric center yield measurable optical activity in polymers. As a result, optically active polymers were prepared from optically active monomers when conditions were used which preserved the asymmetry. It was also possible to form optically active polymers with the aid of optically active initiators.

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3 Molecular Weights of Polymers

3-1. Colligative Property Measurement

When we deal with small molecules, glucose, for example, we can readily establish molecular weight by calculation and by experimental means. This is due to the fact that each molecule is composed of $C_6H_{12}O_6$. But when we deal with a polymer of, say, glucose $+C_6H_{12}O_6+_n$, we may not be able to establish the molecular weight precisely. This is because n usually denotes an average in all but a few biological polymers. That is to say, with only a limited exception, the molecular chains in any given sample of polymers will vary in length. The reason for this is that in the syntheses, whether by chain propagation or in stepwise condensation, the extent of the chain growth is usually governed by purely random events. So the result is that the lengths of chains vary.

The methods available to us for determining these average molecular weights are usually physical, although in certain cases chemical approaches are possible also. The chemical approaches are based on reactions with functional groups, should such be available on the polymer chains. There is a limitation here, however, because of the fact that in order to provide a direct measure of the number of molecules present these must also occur at the chain ends. On occasion one can employ preparative procedures, resulting in the introduction of hetero atoms such as sulfur or halogen or others during termination of chain growth. Then an elemental analysis would suffice. Or the chains might be terminated by olefinic links, which can be chemically determined.

Still another limitation arises from the fact that all chemical means usually become impractical for macromolecules of molecular weight beyond 25,000. When we determine the molecular weight by end-group analysis we are effectively counting the number of molecules and measuring their average molecular weights. Thus we are determining the *number average molecular weight*.

End-group determinations may also afford useful information about the structure of the polymer. Or at times it is possible to study the mechanism of

polymerization when chemical end-group analysis is coupled with physical measurements of molecular weight.

The various physical methods available today include (1) ebullioscopy, (2) cryoscopy, (3) osmotic pressure measurements, (4) light scattering, (5) ultracentrifugation, and (6) gel permeation. All these techniques have one thing in common, in that the measurements are carried out on solutions of polymers. Furthermore, all but gel permeation require that the results be extrapolated to infinite dilutions for rigorous fulfillment of the requirements of theory, which rest upon the fact that no chain entanglements or interactions between polymer or solute and solvent occur. These conditions are even harder to fulfill for macromolecules than for low-molecular-weight species, for they will exhibit deviations from ideality at remarkably low concentrations—hence the need to reduce results to infinite dilution. Or, one can put this in other words by saying that the various physical methods depend essentially on the evolution of thermodynamic properties of the solution, or the kinetic behavior, or a combination of the two.

Additional light can be shed on reasons for working at high dilutions from considerations of the nature of solutions of randomly coiled chain molecules of high molecular weight. A polymer molecule may be approximated by a spherically symmetrical statistical distribution of chain elements about its center of gravity. The volume encompassed by this distribution may be many times the actual molecular volume, with the result that an individual large polymer molecule can exert an influence many times its molecular volume. This will depend, of course, on interaction between polymer elements and the medium in which the polymer is dissolved. Obviously, any chain entanglement resulting from higher concentrations will lead to further deviation from ideality.

To put this differently, all the physical methods presently used for molecular-weight determinations of polymers require that the property measured contribute individually, that is, additively, and that contributions due to interactions between pairs (or clusters) of molecules be negligible. Only if the solution is sufficiently dilute to permit the polymer molecules to occupy separate portions of the volume without any appreciable amount of overlapping will a satisfactory approach be assured. Thus arises the need to work with concentrations below 1 % and in many cases down to several tenths of 1 %.

The relation between colligative properties and molecular weight for infinitely dilute solutions rests upon the fact that the activity of the solute in a solution becomes proportional to its mole fraction.

We have already mentioned one method of expressing molecular weight of polymers—the number average molecular weight. Mathematically this can be expressed as a summation,

$$\overline{M}_n = \frac{w}{\sum_{i=1}^{\infty} N_i} = \frac{\sum_{i=1}^{\infty} M_i N_i}{\sum_{i=1}^{\infty} N_i}$$

It is the sum of the weights of the individual molecules divided by their total number. Each molecule present contributes equally.

Another way to express the molecular weight is to express it as a sum of fractional weights that each molecule in a given sample contributes to the average according to the ratio of its weight to that of the whole sample. This is a *weight average molecular weight*,

$$\overline{M}_w = \frac{\sum_{i=1}^{\infty} M_i^2 N_i}{\sum_{i=1}^{\infty} M_i N_i}$$

To illustrate the differences between number average and weight average molecular weights, let us imagine that we have five molecules with weights of 2, 4, 6, 8, and 10. The number average molecular weight of these molecules will be

$$\overline{M}_n = \frac{2}{5} + \frac{4}{5} + \frac{6}{5} + \frac{8}{5} + \frac{10}{5}$$

$$= 6$$

but the weight average will be

$$\overline{M}_w = \frac{2^2}{30} + \frac{4^2}{30} + \frac{6^2}{30} + \frac{8^2}{30} + \frac{10^2}{30}$$

$$= 7.33$$

As mentioned, end-group analysis leads to number average molecular weights. Also measurements of osmotic pressure, and use of ebulioscopy and cryoscopy, lead to number average molecular weights because these methods are also means for counting molecules, as each molecule contributes equivalently to the measured effect.

But when we use light-scattering measurements, the larger molecules contribute more than the smaller ones and each molecule actually contributes according to its size. So what is obtained is the weight average molecular weight.

It must be understood that the greater the molecular-weight distribution, the greater will be the disparity between molecular-weight averages. The ratio $\overline{M}_w/\overline{M}_n$ is the measure of such a disparity or polymeric dispersity. When all chains are of equal length, then $\overline{M}_w/\overline{M}_n = 1$ and we have a hypothetical monodisperse polymer.

Because the greater the size of the chains, the more they will affect viscosity of solutions, correlations of the viscosities of solutions of linear polymers to their molecular sizes have been established. This can be expressed as *viscosity average molecular weight*,

$$\overline{M}_\eta = \left(\frac{\sum_{i=1}^{\infty} M_i^{\beta+1} N_i}{\sum_{i=1}^{\infty} M_i N_i} \right)^{1/\beta}$$

(Sometimes $\overline{M}_v$ is used in place of $\overline{M}_\eta$ to denote viscosity average molecular weight.) In this equation, β is a constant. When $\beta = 1$, the expression becomes the one for the weight average molecular weight. But usually for linear polymers β is such that $\overline{M}_\eta$ comes to within 20% of $\overline{M}_w$.

Ultracentrifugation yields the *sedimentation average molecular weight.* It is expressed

$$\overline{M}_z = \frac{\sum_{i=1}^{\infty} M_i^3 N_i}{\sum_{i=1}^{\infty} M_i^2 N_i}$$

Only when there is *one* molecular species, M_i, will

$$\overline{M}_n = \overline{M}_w = \overline{M}_z$$

$\overline{M}_w$ is particularly sensitive to higher-molecular-weight species, whereas $\overline{M}_n$ is more sensitive to the lower end of the molecular-weight distribution. If equal weights of molecules with $M_1 = 10{,}000$ and $M_2 = 100{,}000$ are mixed, then $\overline{M}_w = 55{,}000$ and $\overline{M}_n = 18{,}200$. On the other hand, if equal numbers of molecules, each of $M_1 = 10{,}000$ and $M_2 = 100{,}000$, are mixed, then $\overline{M}_w = 92{,}000$ and $\overline{M}_n = 55{,}000$. $\overline{M}_w$ is always greater than $\overline{M}_n$.

With respect to the specific methods mentioned, we shall discuss them only briefly, because this subject is the domain of the analytical and physical chemistry. The advanced student is encouraged to consult appropriate references.

3-2. Ebullioscopy

Ebullioscopy, or boiling-point rise, is applied to macromolecules in the same manner as to low-molecular-weight compounds (*1*). Here one measures the temperature difference of solution required to restore the vapor pressure to its equilibrium value at the boiling point of pure solvent. The big limitation of this method is the fact that ΔT_b becomes increasingly smaller with increase in molecular weight. As a result, this method is limited by the efficiency of the temperature-sensing devices. The uppermost limits appear to be somewhere in the molecular-weight ranges of 40,000 to 50,000. This can be seen from the fact that a polymer of molecular weight 20,000 in a 1% solution might show a temperature change of 0.002°C. The development of differential thermistors capable of sensing temperature changes in the range 1×10^{-4}°C (*2*) has, of course, helped the accuracy of the method. The thermodynamic expression for this boiling-temperature to molecular-weight relationship is

$$\left(\frac{\Delta T_b}{C}\right)_{C=0} = \frac{RT^2}{\rho \, \Delta H_b M}$$

Note that the concentration C must be extrapolated to zero for the relationship to hold.

3-3. Cryoscopy

The freezing-point-depression method as applied to molecular-weight determination of polymers is very similar to that for small molecules. All the limitations mentioned for ebulliometry apply here as well (*1*). Thermodynamically the relationship is expressed

$$\left(\frac{\Delta T_f}{C}\right)_{C=0} = \frac{RT^2}{\rho \Delta H_f M}$$

3-4. Osmotic Pressure

A very useful method for determining number average molecular weights is based on measuring osmotic pressure (*3*) of dilute solutions. Although osmotic pressures were measured successfully by various investigators on solutions in which the molecular weights of the solutes ranged from 180 to 4,000,000, the practical range of this method is from 6000 to approximately 1,000,000.

The principle is based on the fact that when a pure solute is placed on one side of a semipermeable membrane and a solution on the other, pressure (osmotic) develops from the pure solvent side. This pressure can be attributed to the tendency of liquids to equilibrate their concentrations. This pressure was found by van't Hoff (*1*) to be proportional to the molecular size of the solute, decreasing with the increase in molecular weight. It is interesting to note that van't Hoff referred to this procedure as a method of counting the number of dissolved molecules by measuring the osmotic pressure of solution.

He expressed this relationship for small molecules as

$$M = \frac{RT}{\pi/C}$$

where π is the osmotic pressure, C the concentration, M the molecular weight, R a constant, and T the temperature. But, again, for this relationship to be valid for macromolecules it must be reduced to infinite dilution,

$$\overline{M}_n = \frac{RT}{(\pi/C)_{C=0}}$$

So several measurements are taken at various concentrations and the value of π/C is extrapolated to zero concentration as demonstrated in Figure 3-1. The value of X found from the plot is used for π/C in the van't Hoff equation to find $\overline{M}_n$.

Today there are a number of methods for measuring osmotic pressure. They generally fall into two categories, the static method and the dynamic method.

In the static approach the pressure is balanced by the head that develops in a capillary tube. The height of the head is measured and the density of the solution

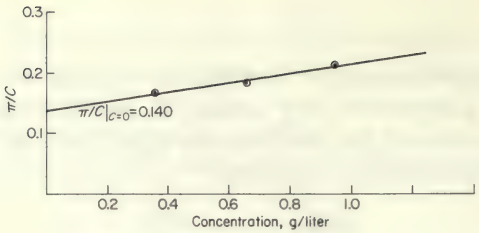

Figure 3-1. Plot of π/C vs. C.

is assumed to be approximately that of the solvent. The osmometer takes anywhere from 1 to 24 hours to equilibrate. The length of equilibration can be a source of error, as the low-molecular-weight species might diffuse through the semipermeable membrane.

The dynamic method consists of applying an external pressure of measurable magnitude so that there will be no developing head. Several high-speed automatic membrane osmometers are now commercially available. One such instrument is shown in Figures 3-2, 3-3, and 3-4. This and other instruments utilize a servomechanism to detect solvent flow through the membrane and to provide hydrostatic head balancing for osmotic pressure to prevent appreciable solvent flow.

It appears that with the dynamic method, permeation, which is time-dependent, is not as great a factor as with the static method.

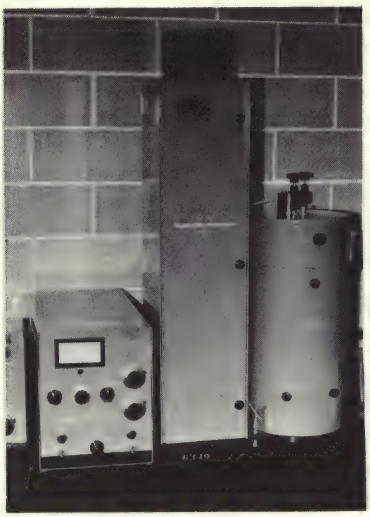

Figure 3-2. Commercial high-speed osmometer, external view. (Courtesy of the F. and M. Scientific Co.)

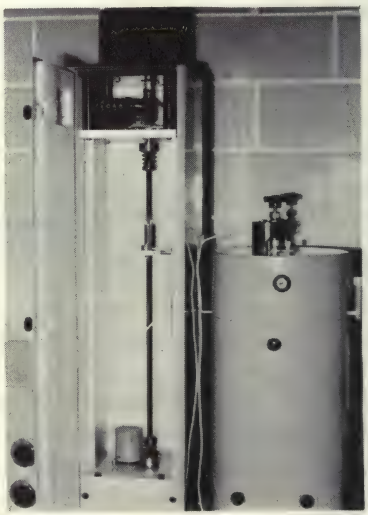

Figure 3-3. Commercial high-speed osmometer, internal view, showing the servo-driven elevator and solvent reservoir. (Courtesy of the F. and M. Scientific Co.)

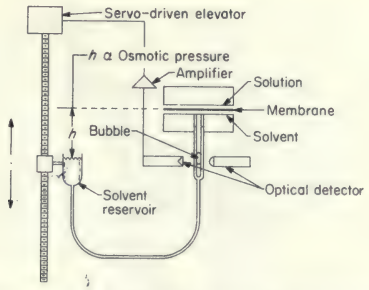

Figure 3-4. Schematic diagram of the construction principle of the high-speed osmometer. (Courtesy of the F. and M. Scientific Co.)

3-5. Isothermal Distillation

Several vapor-pressure osmometers, based on the nonequilibrium vapor-pressure-lowering method, measured thermoelectrically, are commercially available. The basis for this method is the small temperature difference resulting from different evaporation rates of solvent and solution occurring in an atmosphere saturated with solvent vapor. It is assumed that the temperature differences are proportional to the differences in chemical potentials between pure solvent and solvent in solution. This proportionality relates the thermodynamic properties of the solution to the temperature difference established by transport process. Where tested this assumption appears valid, but it needs more proof (*4*).

The manufacturers of the equipment claim $\pm 1\,\%$ accuracy in the 5000 number average range. (One such commercially available unit is illustrated in Figures 3-5 and 3-6.) These claims appear perhaps somewhat exaggerated. With the

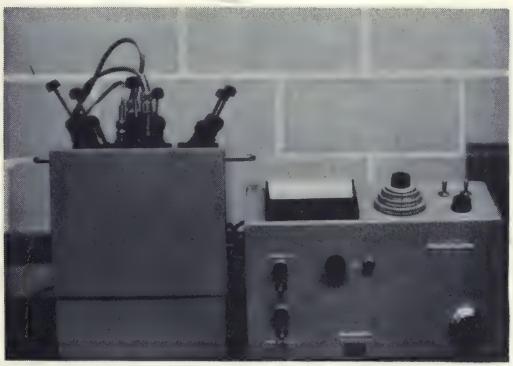

Figure 3-5. Commercially available unit for measuring molecular weights by the isothermal distillation method. This illustration shows the vapor chamber on the left and the controlling and measuring unit on the right. (Courtesy of the F. and M. Scientific Co.)

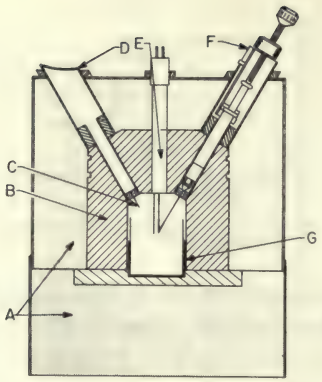

Figure 3-6. Schematic diagram of the vapor-phase osmometer shown in Figure 3-5, showing the internal details of the vapor chamber. A, foam; B, aluminum block; C, chamber; D, syringe guide; E, thermistor probe; F, syringe in down (loading) position; G, solvent cup and wick. (Courtesy of the F. and M. Scientific Co.)

increase in molecular weight the accuracy decreases rapidly, and it seems doubtful that the method is very reliable in molecular-weight ranges beyond 10,000.

The thermodynamic relationships of the change in temperature to molality is

$$\Delta T = \frac{RT^2}{\lambda 100} m$$

where m is the molality of the solution and λ is the heat of vaporization per gram of solvent.

3-6. Light Scattering

So far we have discussed methods useful for the number average molecular-weight determinations. Now, let us turn to a very useful method for determining the weight average molecular weight, based on measuring the scattering of light (*5*).

As light passes through any material medium it loses energy. The molecules of a gas or liquid give the light a certain graininess. Each molecule excited by a beam of light acts like a tiny antenna, picking up energy and reradiating secondary light waves (of the same frequency) in all directions. This phenomenon is defined in a pure liquid as *turbidity*. Any solute dissolved in this liquid will contribute additional scattering. This additional scattering should be proportional to the number of molecules added. In addition, molecules of different sizes will respond differently to light waves of a given frequency. So, to count the molecules, a way must be found to evaluate the unknown amplitude factor. This can be accomplished by measuring the refraction of the light (or bending)

beam which enters it from the air. The amount of change of the refractive index of a liquid is proportional to the number of molecules dissolved in it and the amplitude of electronic vibrations. Whereas increase in scattering of light is proportional to the square of the amplitude, change in refractive index is directly proportional to the amplitude. This measurement leads to two equations which can be solved to give the number of molecules.

The mathematical relationship for the amplitude of the scattered light to the mass of the molecules can be expressed as

$$\tau = \sum_{i=1}^{\infty} \tau_i = H \sum_{i=1}^{\infty} C_i M_i = H_C \overline{M}_w$$

where τ is the scattered light, C the concentration, M the molecular weight, and H the proportionality constant. Or it can be expressed as

$$\frac{H_C}{\tau} = \frac{1}{\overline{M}_w} + 2B \qquad \text{at } C = 0, \theta = 0$$

where θ is the angle from the main beam of light. The $2B$ expression is merely a correction factor for the instrument used.

To determine H we must turn to refractive-index measurements, because H can be expressed in terms of refractive-index change:

$$H = \frac{32\pi^2 n_0^2 (dn/dc)^2}{3\lambda^4 N_0}$$

where π is the constant 3.214, n_0 the refractive index of pure solvent, dn/dc the change in refractive index with concentration, λ the wavelength of light used (usually = 546 mμ, green light, or 436 mμ, blue light), and N_0 is Avogadro's number.

For macromolecules below 100,000 molecular weight, it is sufficient to extrapolate to zero concentration to obtain the value of H_C. But for molecular weights beyond 100,000, both extrapolation to zero concentration and zero angle of scattering is necessary. Zimm introduced an approach that makes use of data taken over as large an angle range as possible, plotting the data in such a way as to achieve intercept of zero angle and zero concentration. Thus $C \to 0$ and $\theta \to 0$. A typical Zimm plot would look as shown in Figure 3-7.

It is very important that light-scattering measurements be carried out on very pure solutions, free of dust or other extraneous particles, because the scattering from any extraneous material such as dust may outweigh the scattering from the polymer molecules. Thus ultracentrifugation is a method sometimes employed to achieve maximum clarification (*6*). When this is not available, thorough filtration through a very fine pore filter might be used.

Although light scattering is an almost standard way of determining weight average molecular weights, difficulties still exist in determinations carried out on solutions of copolymers. It was shown that too high a molecular weight will

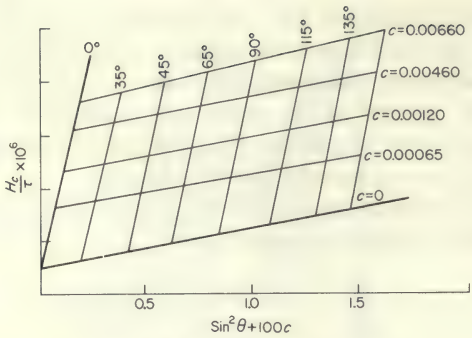

Figure 3-7. A typical Zimm plot.

result, owing to fluctuations in chain compositions, with the magnitude of this effect increasing rapidly as the absolute value of the refractive-index increment approaches zero. Thus one may have to correct from the apparent molecular weight to the actual one for chains containing much heterogeneity.

In general, though, light scattering can be used on polymers of molecular weight from 10,000 to 10,000,000. Several commercial turbidimeters specially designed for light-scattering measurements are available. One such unit is shown in Figures 3-8, 3-9, and 3-10.

3-7. Viscometry

Solution viscosity is basically a measure of size or extension in space of polymer molecules. It is related (empirically) to molecular weight, but only for linear polymers. Owing to its ease of use and fairly good correlation with molecular weights, it is a very useful tool.

The experimental procedure consists of measuring the efflux time, t, it takes a given volume of polymer solution to flow through a capillary tube and relating

Figure 3-8. Commercially available light-scattering photometer, external view. (Courtesy of the Phoenix Precision Instrument Co.)

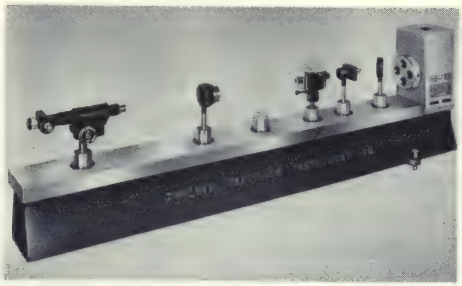

Figure 3-9. Differential refractometer used in conjunction with the photometer of Figure 3-8. (Courtesy of the Phoenix Precision Instrument Co.)

it to the corresponding efflux time t_0 for the solvent. This leads to the following expressions:

Relative viscosity: $\eta_r = \eta/\eta_0 = t/t_0$
Specific viscosity: $\eta_{sp} = \eta_{rel} - 1$
Reduced viscosity: $\eta_{red} = \eta_{sp}/C$
Inherent viscosity: $\eta_{inh} = \ln \eta_{rel}/C$
Intrinsic viscosity: $[\eta] = (\eta_{sp}/C)_{C=0}$

where C is the concentration.

The intrinsic viscosity being independent of concentration by virtue of extrapolation to zero concentration can be used for molecular-weight determinations.

Mark–Houwink expressed this in the relationship

$$[\eta] = K'M^a$$

where K' and a are constants determined from a double logarithmic plot of intrinsic viscosity and molecular weight. This empirical relationship is valid only for linear polymers, which is a limitation of the method.

As already stated, in practical cases $\overline{M}_\eta$ is often within 20% of $\overline{M}_w$.

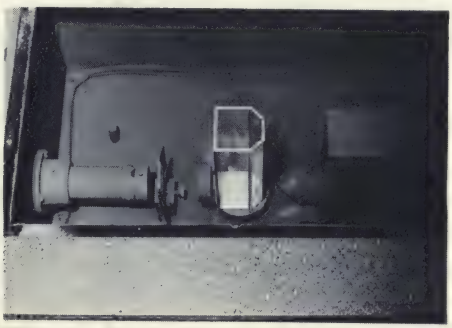

Figure 3-10. Internal view of the light-scattering photometer shown in Figure 3-8. The cell can be seen in the center and between the light source on the left and the photosensitive cell on the right.

3-8. Ultracentrifugation

When a polymer solution is placed in a cell of a high-speed centrifuge, the polymer molecules tend to distribute themselves during rotation perpendicularly to the axis of the rotation throughout the cell and in accordance with the mass of the individual polymer molecule (*7*). At constant force the larger molecules will move rapidly toward the periphery, and at equilibrium the largest molecules will be found nearest the periphery. By passing a light beam parallel to the axis of rotation and perpendicular to the axis of the cell and by using this light beam to measure the refractive index, concentration of the polymer in any given section can be measured. This allows determination of the velocity of the molecular movement toward the periphery or the gradient at equilibrium.

The mathematical relationship that relates the force acting upon the particle to its molecular weight is

$$F = m(1 - \bar{v}\rho)X\omega^2$$

where X is the distance from the axis of rotation, m the particle mass, $\bar{v}$ the specific volume of the particle, ρ the density of the medium, and ω the angular velocity.

Billmeyer (*4*) compared the utility of the light-scattering method to ultracentrifugation by presenting a table of results obtained by both methods (Table 3-1).

TABLE 3-1

Weight Average Molecular Weight by Various Methods[a]

Sample	$\overline{M}_w$ by light scattering	$\overline{M}_w$ by ultracentrifugation
Linear polyethylene	144,000	126,000
Poly(methyl methacrylate)(fraction)	148,000	159,000
Whole polymer of poly(methyl methacrylate)	490,000	524,000

[a] From Reference *4*.

3-9. Gel-Permeation Chromatography

Any discussion about methods for molecular-weight measurements or about molecular sizes and their distributions must also include consideration of a new rapidly evolving method—gel-permeation chromatography. The principle is based on a special type of liquid-solid elution-column chromatography involving the permeation of solute molecules into rigid gel particles. The larger the molecules, the less they are capable of penetrating the small voids of the gels, with the result that they are eluted first and a separation by size is accomplished. Thus the method is a simultaneous measurement of molecular sizes and their distributions (*8*).

The gel can be made up of a variety of cross-linked polymers, although the materials currently available commercially are prepared from styrene cross-linked in the presence of diluents, developed by Moore and Hendrickson. Elution curves of single components were found to be symmetrical, fitting closely the normalized probability function (*9*, *10*). Furthermore, Moore and Hendrickson obtained calibration curves for polystyrene and polyglycols that were not affected by column temperature changes or by changes in other good solvents as eluents. Rapid repetitive molecular-weight-distribution data were obtained on polymers using solvents compatible with these gels (*9*,*10*).

Maley (*11*) reported that the technique has been tested on a wide variety of polymers, including those with molecular weights above 10^6 and those with molecular weights of 200–300. What still remains to be shown, however, is whether this technique applies in the same manner to branched as to linear polymers, and more so, how the method applies to copolymers with high composition dispersity. The equipment consists of several stainless-steel $\frac{3}{8}$-inch tubes, 4 feet in length, filled with about 25 cc of the gels. Several columns are used, differing in the pore sizes of the gels. The flow rate is usually set at 1 cc per min, with the pressure drop of a typical column reported to be at 10 psig. The schematic diagram of the equipment is shown in Figures 3-11 and 3-12. Two typical distribution curves are reproduced in Figures 3-13 and 3-14.

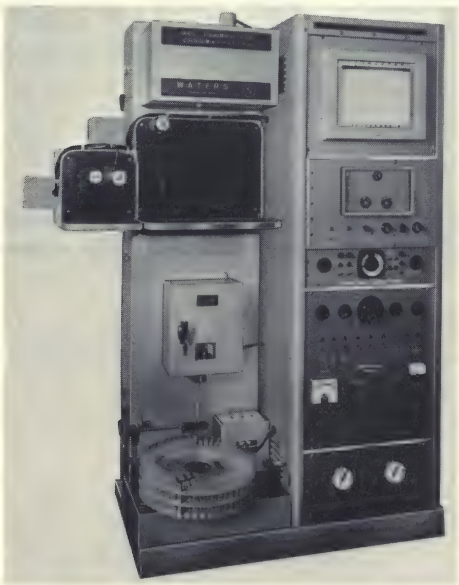

Figure 3-11. Commercially available gel-permeation chromatograph. (Courtesy of Waters Associates.)

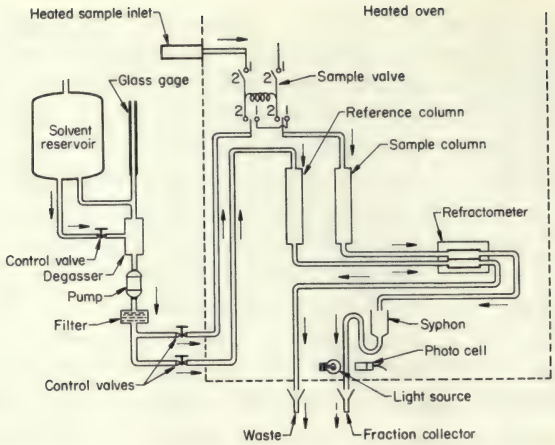

Figure 3-12. Schematic diagram of the principle of construction used in a commerical unit offered for gel-permeation studies. Only one sample column is shown, although usually from two to four columns are used. (Courtesy of Waters Associates.)

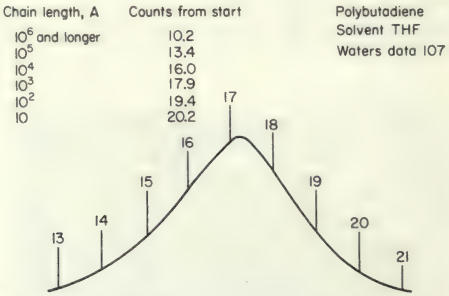

Figure 3-13. Differential distribution curve for a polybutadiene run in tetrahydrofuran, obtained with the Water's gel-permeation equipment. (Courtesy of Waters Associates.)

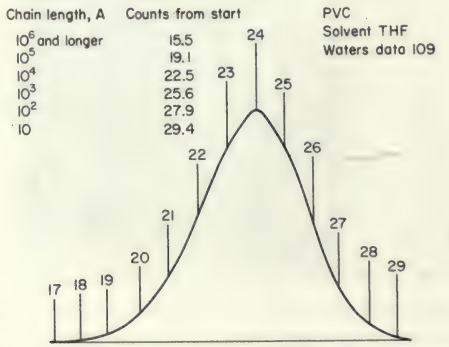

Figure 3-14. Differential distribution curve for a poly(vinyl chloride) run in tetrahydrofuran. (Courtesy of Waters Associates.)

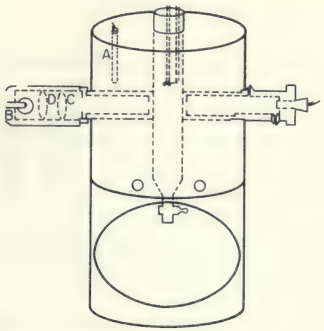

Figure 3-15. Cell for turbidity measurements. A, temperature-sensing element; B, light source; C, iris diaphragm; D, lenses. (Courtesy of the *Journal of Polymer Science.*)

3-10. Thermal Gradient–Turbidity Technique

Another very interesting technique for measuring molecular-weight distributions rapidly was reported by Gamble and co-workers (*12*). The method is an extension of a photoelectric turbidimetric technique reported by Taylor and Tang. Relative changes in turbidity of polymer solutions are measured as a function of temperature. An *XY* recorder allows the plotting of turbidity changes with temperature. A parameter determined from the plot is correlated with a measure of molecular-weight distribution determined on known samples for each specific type of polymer by another means. Using such correlation, unknown samples can be analyzed. The equipment is shown in Figures 3-15 and 3-16.

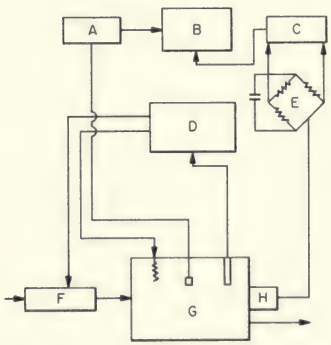

Figure 3-16. Schematic diagram of the instrumentation used in the thermal gradient–turbidimetric technique. A, *Y* amplifier; B, recorder; C, *X* amplifier; D, temperature programmer; E, photo bridge; F, solenoid switch for water; G, turbidity cell; H, photoelectric sensing element. (Courtesy of the *Journal of Polymer Science.*)

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Part II

POLYMERIZATION REACTIONS—MECHANISMS

4

Addition Polymerization: Mechanism of Free-Radical Polymerization

4-1. Chemistry of Vinyl Polymerization

The free-radical-initiated polymerization process is generally limited to forming macromolecules from monomers possessing olefinic links:

In this typical chain reaction, one act of initiation may lead to the addition of thousands of monomers. For consideration of the reaction mechanism, this act can be separated into four steps:

1. *Initiation.* In the first step an initiator undergoes decomposition and becomes a source of radicals. Then these newly formed radicals react with the monomer to initiate chain growth,

$$\underset{(initiator)}{R{-}R} \rightarrow \underset{(radical)}{2R\cdot}$$

$$\underset{(monomer)}{R\cdot + M} \rightarrow \underset{(new\ radical)}{RM\cdot}$$

2. *Propagation.* Chain growth proceeds after initiation by continuing addition of monomers to growing chains,

$$RM\cdot + M \rightarrow RMM\cdot$$

$$RMM\cdot + M \rightarrow RMMM\cdot$$

$$RMMM\cdot + M \rightarrow RMMMM\cdot \quad \text{etc.}$$

3. *Termination.* Two growing chains, having terminal radicals, combine to end chain growth. This is known as *termination by recombination*,

$$RM(M)_nM\cdot + RM(M)_mM\cdot \rightarrow RM(M)_nMM(M)_mMR$$

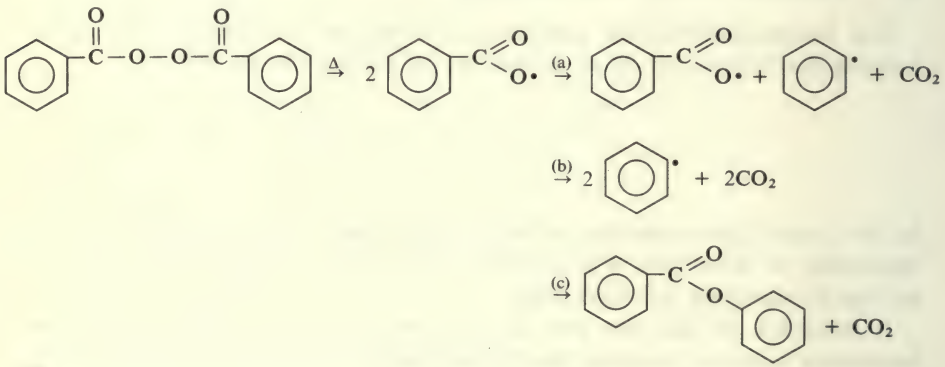
4. *Transfer.* The active radical site is transferred to another molecule, often by the mechanism of abstraction of a proton or some other atom from another molecule,

$$RM(M)_nM\cdot + R'H \rightarrow RM(M)_nH + R'\cdot$$

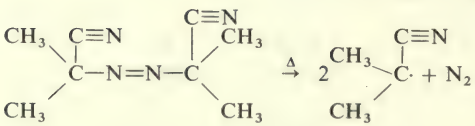
Formation of initiating free radicals can be achieved from chemical sources, such as free-radical initiators, or from ultraviolet light (which can lead to the conversion of olefinic bonds into radicals via the excited state). It is also possible to achieve this by thermal initiation.

4-2. Chemical Initiation

Chemical initiation depends upon the presence in the reaction medium of molecules capable of generating or decomposing into free radicals at certain temperatures. To these belong various azo compounds, peroxides, and hydroperoxides. Typical decomposition can be represented as



or



It should be obvious that success in such reactions depends upon the readiness with which initiators will decompose into these radicals as well as upon the ability of radicals to react with monomers. This decomposition of initiator into radicals, which starts chain growth, is usually defined as initiator efficiency and expressed in terms of fragments from the initiator that start polymer chains.

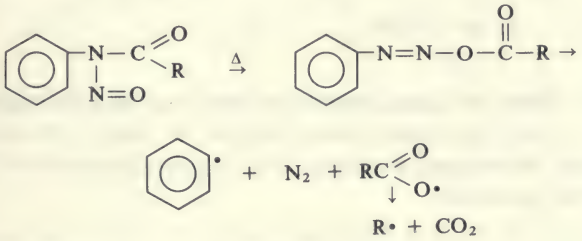
The primary radicals from initiator decomposition may differ in their efficiencies of chain initiation from secondary ones, or vice versa. It is, therefore, important to be aware of all reactive species present and the respective kinetics in a given reaction. The reactivity of olefins toward free radicals is a function of both the nature of the attacking radical and the energy necessary to accomplish

bond rupture (*1*). Much effort has gone into studying initiator efficiencies (*2–8*).

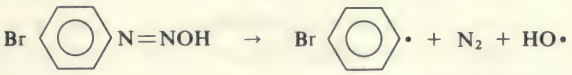
Today we have an impressive number of molecules which are efficient generators of radicals and potent initiators for radical polymerizations. Examples of such efficient initiators are:

1. *Nitrogen-bearing compounds:*

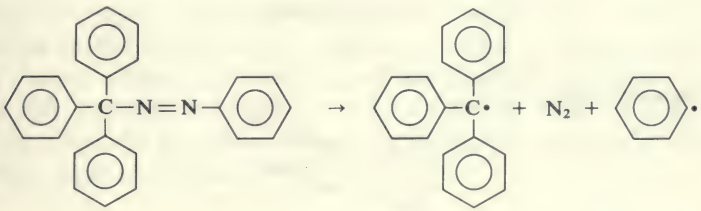
a. N-nitrosoacylanilide:



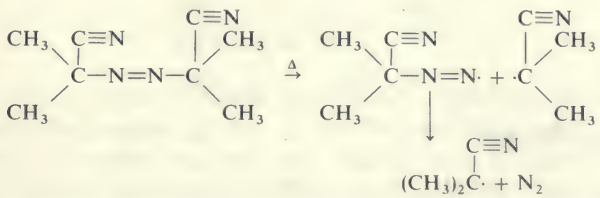
b. *p*-Bromobenzenediazohydroxide:



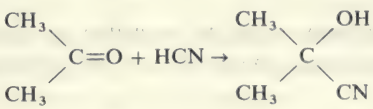
c. Triphenylazobenzene:

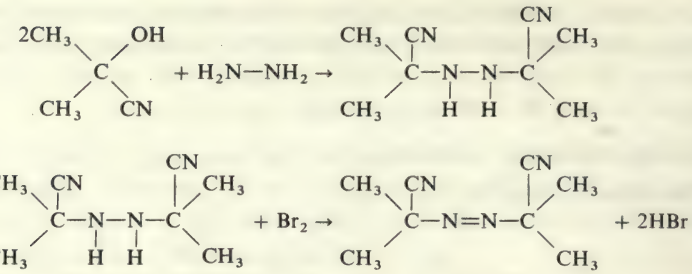


d. Aliphatic azobisnitriles, such as



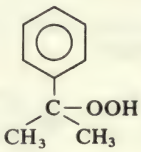
This material is available commercially. Its synthesis is described by Thiele and Hauser (*9*):



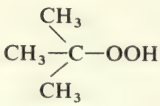


2. *Peroxides:* These are quite numerous and can be subdivided into five classes: alkyl or aryl hydroperoxides, dialkyl or diaryl peroxides, diacid peroxides, peroixy esters, and peracids. Some typical examples of these are:

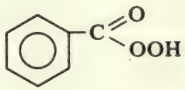
a. Cumene hydroperoxide:



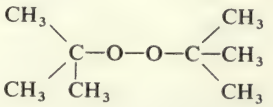
b. *t*-Butyl hydroperoxide:



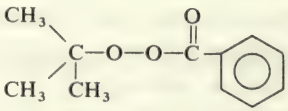
c. Perbenzoic acid:



d. Ditertiarybutyl peroxide:

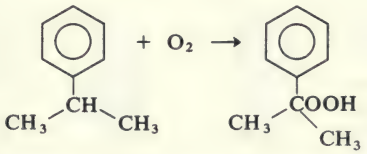


e. *t*-Butylperbenzoate:



In general, organic peroxides may be regarded as derivatives of hydrogen peroxide obtained by replacing one or both of the hydrogen atoms by organic radicals.

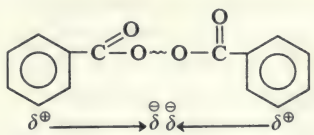
The hydroperoxides are prepared by (1) the general method of alkylating hydrogen peroxide with alkyl halides, alkyl sulfate, or alcohols in the presence of strong acids, (2) by controlled oxidation of hydrocarbons with molecular oxygen,



or (3) by addition of oxygen to Grignard reagents,

$$RMgX + O_2 \xrightarrow{HOH} ROOH + MgXOH$$

Decomposition of these polymerization initiators is, of course, temperature-dependent, or the rate varies with temperature. But the rate is also influenced by the surrounding medium, such as solvent. So, to carry out an efficient reaction, the proper choice must be made of initiator as well as reaction conditions. Much research has gone into various parameters involved in such reactions. For example, Bartlett and co-workers (*10–14*) have investigated the mechanism of decomposition of peresters. Another typical example of such an investigation is the work of Martin (*15*), who investigated the mechanism of thermal decomposition of di-*t*-butyl diperoxycarbonate. As a result, it is now possible to correlate the chemical structure of the initiator with its expected behavior. The effect of various strains and inductive effects upon the peroxide link in the molecule, for instance, is relatively easy to predict. Thus, for example, in benzoyl peroxide, the two benzoate groups are dipoles, attached in such a way as to always repel each other,



Cleavage of the bond releases electrostatic repulsion between the two dipoles. Electron-donating groups on the benzene ring, such as *p*-methoxy, will, therefore, increase the negative charge and accelerate the rate of spontaneous fission. Electron-attracting groups, on the other hand, such as *p*-cyano or *p*-nitro, will decrease the negative charge on the peroxide oxygens and therefore lower the rate of cleavage.

A quantitative treatment of the effects of substituents on the rate of spontaneous cleavage of substituted peroxide was given by Swain (*16*) in terms of the Hammett equation (*17*), $\log(k/k_0) = \rho\sigma$; see Table 4-1. Two types of peroxide cleavage are possible: heterolytic and homolytic.

TABLE 4-1

Cleavage of Substituted Dibenzoyl Peroxides in Benzene[a]

Substituents	$K_i \times 10^3$	$\log k/k_0$	$\sigma_1 + \sigma_2$
p,p'-dimethoxy	7.06	0.447	−0.536
p-methoxy	4.54	0.255	−0.268
p,p'-dimethyl	3.68	0.164	−0.340
Dibenzoyl	2.52	0.000	0.000
m,m'-dichloro	1.58	−0.203	0.746
p,p'-dicyano	1.22	−0.314	1.30

[a] From Reference *16*; reproduced with permission of the American Chemical Society.

Cleavage of peroxides into ions rather than radicals by separation into unlike charged particles is called *heterolytic cleavage*,

$$R^{\oplus} + :\overset{\ominus}{O}-O-R' \rightleftharpoons R-O-O-R' \rightleftharpoons R-O-\overset{\ominus}{O}: + R'^{\oplus}$$

Homolytic cleavage is a case of fision into radicals,

$$R-O-O-R' \rightleftharpoons RO\cdot + \cdot OR'$$

Usually all cleavages in the gaseous phase will be homolytic, for they require the least amount of energy. In solution, however, dissociation might tend to be either one of the two, depending upon the natures of the R and R′ groups. Solvation of the resultant ions formed from the cleavage could also be a determinant of the manner in which this cleavage would proceed.

A number of diagnostic tests exist to determine the manner in which compounds R—O—O—R′ will decompose (*18*). Based on these tests, a proper choice of the desired initiation should be possible.

As stated, in considering the radical-forming ability of peroxides, one must also take into account the effect of the surrounding medium. Solvents can influence the rate of peroxide decomposition. This is illustrated in Table 4-2, which gives the half-life of benzoyl peroxide in various solvents.

After cleavage of initiators into primary radicals took place, a number of typical radical chain reactions occur. The solvent present in any reaction medium can enter such reactions, and, in fact, fragments of solvent molecules can be shown to be present among the decomposition products from initiators.

In addition to spontaneous decompositions of initiators into radicals caused by thermal means or ultraviolet light, an induced decomposition of peroxides can also be achieved by various chemical means. These range from reactions with ions to those with molecules and radicals.

TABLE 4-2
Decomposition of Benzoyl Peroxide at 79.8°C in Some Solvents[a]

Solvent	Decomposition, %	
	1 hour	4 hours
Tetrachloroethylene	13.0	35.0
Carbontetrachloride	13.5	40.0
Cyclohexene	14.0	39.5
Methylbenzoate	14.5	41.4
Anisole	14.0	43.0
Chloroform	14.5	43.7
Benzene	15.5	50.4
Acetone	28.5	
Cyclohexane	51.0	84.3
Ethyl benzene	15.0	45.5
Chlorobenzene	18.0	48.5
Nitrobenzene	15.5	49.0
Benzene	15.5	50.4
Toluene	17.4	49.5
Allyl acetate	19.0	
Cumene	20.0	53.3
Carbon disulfide	19.0	
Methylene chloride	24.5	62.2
Ethyl chloride	26.0	64.7
Ethyl acetate	53.5	85.2
Dioxane	82.4	

[a] From Reference *19*. The half-life of some common organic initiators is shown in Table 4-3.

An electron-transfer mechanism appears to be involved in all these reactions. The peroxide, after receiving an additional electron, breaks down to form a radical plus a negative ion,

$$A + ROOR' \rightarrow A^{\oplus} + RO\cdot + R'O^{\ominus}$$

Actually the reaction is probably more complex.

A good example of such a reaction would be decomposition of hydrogen peroxide by ferrous ion:

1. $H_2O_2 + Fe^{\oplus\oplus} \rightarrow HO\cdot + OH^{\ominus} + Fe^{\oplus\oplus\oplus}$
2. $HO\cdot + Fe^{\oplus\oplus} \rightarrow HO^{\ominus} + Fe^{\oplus\oplus\oplus}$
3. $HO\cdot + H_2O_2 \rightarrow H_2O + HO_2\cdot$
4. $HO_2\cdot + H_2O_2 \rightarrow HO\cdot + H_2O + O_2$

Although the ferrous ion is a nucleophilic agent, decomposition is also possible with electron-seeking groups:

1. $ROOH + Ce^{\oplus\oplus\oplus\oplus} \rightarrow Ce^{\oplus\oplus\oplus} + RO_2\cdot + H^{\oplus}$
2. $RO_2\cdot + Ce^{\oplus\oplus\oplus\oplus} \rightarrow R^{\oplus} + O_2 + Ce^{\oplus\oplus\oplus}$

TABLE 4-3
Half-Life of Organic Initiators[a]

Initiator	Half-life, hours			
	50°C	75°C	100°C	150°C
2,4-Dichlorobenzoyl peroxide	17.8	0.76	—	
Lauryl peroxide	54	1.7	0.1	
Caprylyl peroxide	64	1.8	0.1	
Azobisisobutyronitrile	83	2.4	0.12	
Acetyl peroxide	158	4.1	0.2	
Benzoyl peroxide	190	6.7	0.4	—
p-Chlorobenzoyl peroxide	260	9.3	0.5	
t-Butyl peroxyisobutyrate	886	14.2	0.55	
t-Butyl peracetate	—	—	11.0	—
Methyl ethyl ketone peroxide	—	—	16.2	0.17
t-Butyl hydroperoxide	—	—	165	0.3
Di-*t*-butyl peroxide	—	—	218	0.8
Cumene hydroperoxide	—	—	—	25

[a] Data from various sources in the literature.

Dean and Skirrow (*20*) studied the induced decomposition of *t*-butyl hydroperoxide by cobalt ions. They concluded that the mechanism can be expressed as

$$Co^{\oplus\oplus} + ROOH \longrightarrow Co^{\oplus\oplus\oplus} + RO\cdot + OH^{\ominus}$$

$$Co^{\oplus\oplus\oplus} + ROOH \xrightarrow{\text{rapid}} Co^{\oplus\oplus} + RO_2\cdot + H^{\oplus}$$

$$2ROO\cdot \longrightarrow 2RO\cdot + O_2$$

or

$$RO_2\cdot + ROOH \longrightarrow RO\cdot + O_2 + ROH$$

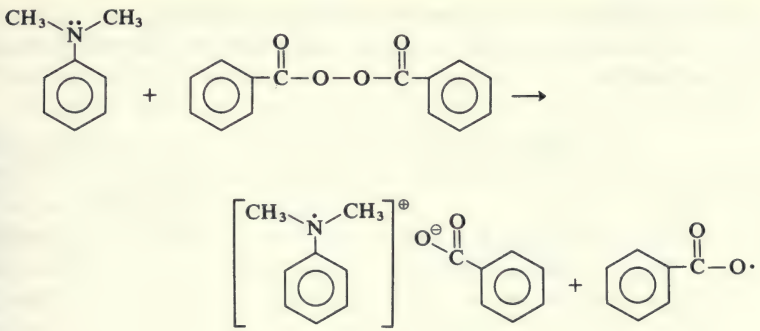
$$RO\cdot + Co^{\oplus\oplus} \longrightarrow RO^{\ominus} + Co^{\oplus\oplus\oplus}$$

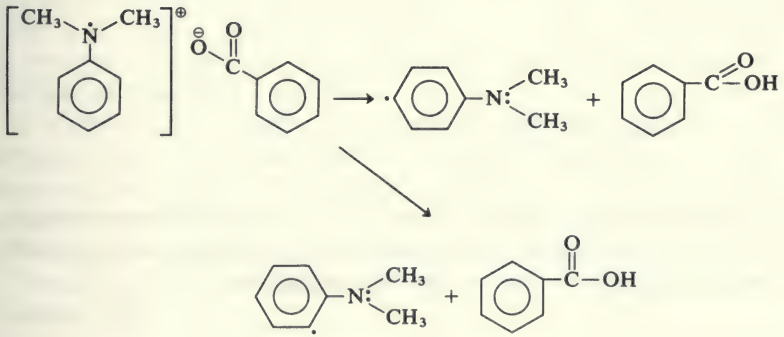
$$RO\cdot + ROOH \longrightarrow ROH + ROO\cdot$$

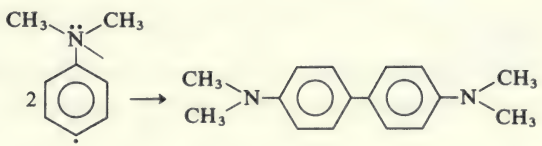
Here *t*-butyl alcohol is the main product.

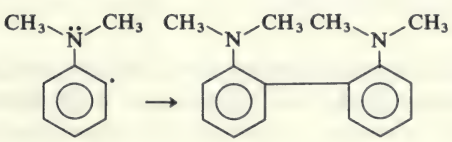
Tertiary aromatic amines can also cause induced decomposition of peroxides. The mechanism of reaction was studied by Horner and Schlenk (*21*), who proposed the following scheme.

During reaction between tertiary aromatic amine and benzoyl peroxide, a transition state occurs in which a transfer of an electron from the unshared pair on the nitrogen takes place. The benzoylate anion then abstracts a proton, yielding a radical:



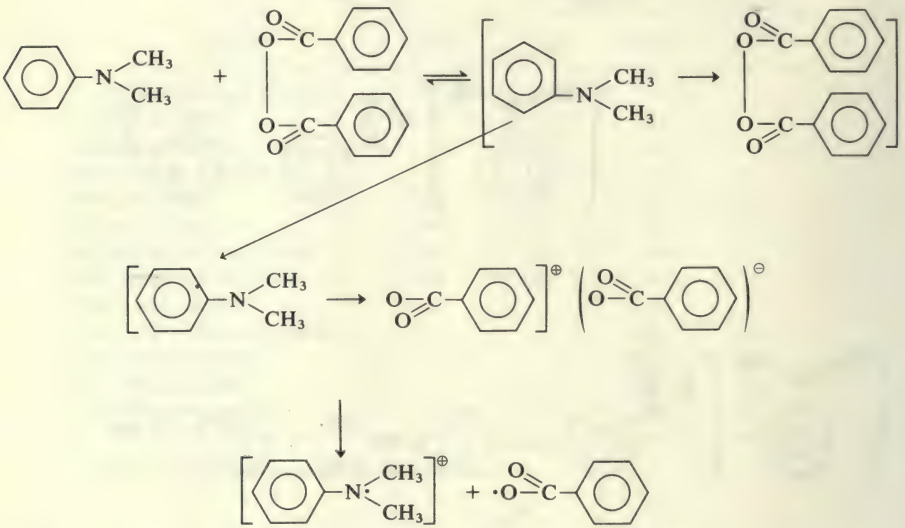






All other radical recombinations are, of course, possible.

An alternative mechanism was assumed by Imoto and Choe (*22*), who suggested the following:



The above scheme can be assumed to represent merely the intermediate step in the Horner-Schlenk mechanism (*21*), except that according to Imoto et al. (*23*) only benzoyl radical can now initiate polymerization.

4-3. Ultraviolet-Light Initiation

When light energy is absorbed by matter, electronic excitations are created (*24*). As a result of these excitations, molecules might break down into radicals and then react with neighboring molecules, bringing about chemical reactions. The energy of excitation, however, might only be given off again through the emission of fluorescence.

Properties of excited atoms and molecules have been investigated by spectroscopic means (*25*, *26*). The general reaction can be expressed as

$$A + h\nu \rightarrow A^*$$

The electron is moved from the ground state to a new orbit corresponding to a higher energy (*27*). Furthermore, in such photoelectric absorption, if the incoming energy is high enough and in excess of the binding energy, the electron of the excited atom can be liberated and can then carry off excess energy of the photon (*28*).

Since all possible energy states of the molecules are regulated by quantum mechanical considerations, it follows that only those light quanta can be absorbed whose energies equal the differences between energy states,

provided the transition between these states is allowed (*29*). Light absorption is, therefore, selective and energy of light absorbed is a function of the molecular structure of the absorbing matter (*30*). In addition to this, one might say that absorption of light of a given wavelength will raise the energy of the absorbing molecule to a particular well-defined energy state. Furthermore, if the molecule is complex, light absorption may often be limited to only one of the functional groups present.

Electronically excited states formed by direct absorption of light are normally singlet states, while those formed by intersystem crossing are triplet states (*31*). Structurally the triplet state is distinguished from the singlet state by inversion of the spin of the excited electron (*32*). Briefly, this means that in stable molecules the electrons are normally grouped in pairs, in each of which two electrons have opposite spins. Excitation to an excited singlet state results in translation of one of the electrons to a higher-energy orbit, but without change in direction of the spin. However, when excitation involves both transfer of an electron to a higher orbit and an inversion of the spin of this electron, then this becomes an excited triplet state. The molecule now has two unpaired electrons and can be considered a diradical.

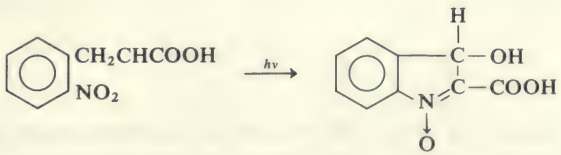
It is interesting to observe in passing that the triplet excited states have longer lifetimes than single excited states (*33*). The lifetime of triplet excited states is apparently influenced by the physical state of the medium and is longest in very viscous or solid systems. Lifetimes of singlet states, on the other hand, are not affected by the nature of the surrounding medium.

The excited molecule returns to the ground state by undergoing one of several reactions (*34*):

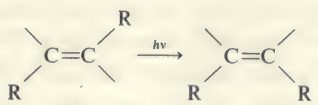
1. Fluorescence:

$$A^* \rightarrow A + h\nu'$$

2. Rearrangement:



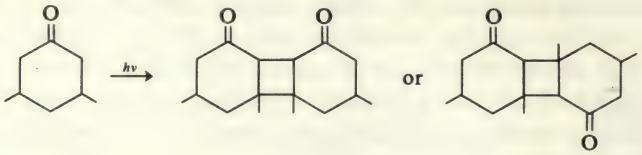
3. Unimolecular reactions:



trans *cis*

Many other examples of this reaction are known, the more familiar ones being perhaps the photochromism of spirans (*35*) and the dissociation of bibenzimidazoles (*36*).]

4. Bimolecular reactions:



5. Energy transfer:

$$A^* + B \rightarrow A + B^*$$

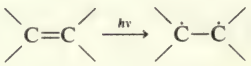
Foerster (*37*) demonstrated one mechanism of energy transfer of this type, probably that of high energy. He showed that singlet states might transfer by a mechanism of dipole-dipole interaction at distances up to 100 A. Hammond (*38*) has demonstrated that triplet states can transfer energy as well. However, here, a collision of molecules is believed necessary. Furthermore, he demonstrated a strong dependence of the reaction course upon the triplet excitation energy of the donor.

If the excited state has sufficient free energy, the molecule may then rupture a covalent bond to give two free radicals. So the following reactions can take place:

1. $A^* \rightarrow \cdot A \cdot$
2. $A^* + M \rightarrow \cdot AM \cdot$
3. $A^* \rightarrow B \cdot + C \cdot$
   or a transfer
4. $A^* + RH \rightarrow AH + R \cdot$

To accomplish bond rupture the energy of excitation must be equal to the bond energy, but frequently more is required, as indicated by kinetic data.

Formation of diradicals from unpairing electrons of carbon to carbon double bonds of olefins was demonstrated by Melville (*39*) and Mochel and co-workers (*40*),



Such a dissociation is often the first step in photochemical reactions and is, therefore, of prime importance to photopolymerization, which concerns the reactions of olefinic compounds. But, to be capable of initiating polymerization, the excited species A* must be energetic and long-lived, particularly where bimolecular collisions are required. For instance, if the reaction is carried out in a liquid media, radicals may be unable to escape through the closely packed molecules that surround them. In this case they might recombine, dissipating the energy of recombination as heat and producing no over-all chemical change. The caging and recombination of free radicals from excited molecules before they have become separated is known as the *Frank-Rabinowitch*, or *cage, effect* (*41*).

In addition, the site in the molecule at which light is absorbed is not necessarily the same site at which bond rupture might take place. Instead, bond cleavage often occurs at the weakest bond. Thus aldehydes and ketones absorb the light characteristic of the carbonyl group but subsequently break at a carbon-to-carbon bond (*42*).

The fact that reactions must be carried out at the absorption frequencies of the molecules is a serious limitation. To overcome it, sensitizers are often employed, as they offer convenience of operating at light frequencies other than those required for excitation of individual monomers. Sometimes the excitation frequency may change as result of cumulative effects, as in compounds with several aromatic groups within the same molecule, or several functional groups, and so on (*43*). If two polar groups are separated from each other, however, even though within the same molecule, they might act independently of each other (*44*).

Hammond (*38*) defines a good sensitizer as a compound that functions efficiently in the following reaction sequence:

1. $S \xrightarrow{h\nu} S^{*1}$

2. $S^{*1} \xrightarrow[\text{crossing}]{\text{intersystem}} S^{*3}$

3. $S^{*3} + A \xrightarrow[\text{transfer}]{\text{energy}} S + A^{*3}$

He further states that in addition to having high efficiency in intersystem crossing and energy transfer, the sensitizer should have other desirable characteristics. Ideally, the sensitizer should absorb strongly at longer wavelengths than those at which the acceptor (A) absorbs. High efficiency in reaction 3 requires that the triplet excitation energy of S be higher than that of A.

Low-molecular-weight ketones and aldehydes can often be used as sensitizers. Photolytic decomposition of acetone (*45*) can be shown as follows:

$$\begin{aligned}
CH_3\overset{\overset{O}{\|}}{C}CH_3 &\xrightarrow{h\nu} CH_3\dot{C}O + \dot{C}H_3 \\
CH_3\dot{C}O &\longrightarrow \dot{C}H_3 + CO \\
2CH_3 &\longrightarrow C_2H_6 \\
2CH_3{-}\dot{C}O &\longrightarrow CH_3{-}CO{-}CO{-}CH_3 \\
\dot{C}H_3 + CH_3{-}\dot{C}O &\longrightarrow CH_3{-}CO{-}CH_3 \\
\dot{C}H_3 + CH_3{-}COCH_3 &\longrightarrow CH_4 + CH_3{-}CO{-}CH_2\cdot \\
\dot{C}H_3 + CH_3{-}CO{-}\dot{C}H_2 &\longrightarrow CH_3{-}COC_2H_5
\end{aligned}$$

The above reaction was written for small-chain ketones such as acetone. Longer-chain ketones react differently (*46*), by yielding olefins (Norrish reaction),

$$CH_3{-}COCH_2{-}CH_2{-}CH_2{-}CH_3 \xrightarrow{h\nu} CH_3{-}CO{-}CH_3 + CH_2{=}CHCH_3$$

Decomposition of aldehydes into free radicals under the influence of ultraviolet light (*47*) can be shown as

$$CH_3—CHO \xrightarrow{h\nu} CH_3\cdot + \cdot CHO$$
$$CH_3\cdot + CH_3—CHO \longrightarrow CH_4 + \dot{C}H_2CO \quad \text{etc.}$$

So acetone and acetaldehyde are often added as photoinitiators.

Peroxides will also decompose (*48*) under ultraviolet light and are also useful as ultraviolet initiators,

$$R—O—O—R \xrightarrow{h\nu} 2RO\cdot$$

One must, of course, avoid addition reactions of peroxides to olefins, which can occur in ultraviolet light, as, for example, the addition of hydrogen peroxide to double bonds (*49*).

There are many other compounds that are useful as radical producers, such as aliphatic azo compounds (*50*), disulfides (*51*), and diazonium salts (*34*).

4-4. Inhibition and Retardation

As mentioned, free-radical intiated polymerization is subject to inhibition and retardation (*52*). Substances that can act as retarders include stabilized radicals capable of reacting with other radicals but incapable of reacting with monomers. Thus, if the retarder reacts with a growing chain, it acts as a typical chain-transferring agent,

$$\sim\!P\cdot + X\cdot \rightarrow \sim\!P + Y\cdot$$

where $\sim\!P\cdot$ is a growing chain, X· a stabilized radical or retarder, $\sim\!P$ a dead polymer chain, and Y the stabilized product from X·.

A molecule with a labile proton, easily abstracted by a radical, may often act as such a transfer agent. If, upon removal of the proton, the newly formed radical is so stable that it is incapable of initiating new chain growth, then it is not really a chain-transferring agent but merely a retarder.

Inhibitors are chemical substances that cause well-defined induction periods, followed by polymerizations at normal rates. Such induction periods are periods during which initiating radicals are consumed in reactions with inhibiting chemical substance at such fast rates that they prevent any reactions with monomers. The result is also the formation of new radicals which are too stable to initiate chain growth. The rate of reaction of an ideal inhibitor must be high enough to cause inactivation of all initiating radicals as quickly as they are formed. So the induction period is the period during which all the inhibitor is consumed. Once consumed, however, the polymerization may proceed and at a normal rate, for the inhibitor is no longer active.

Retarders, on the other hand, remain active throughout the whole course of polymerization. An ideal retarder will exhibit no induction period. Both inhibitors and retarders react with initiating radicals, but the inhibitors react rapidly, whereas the retarders react slowly. As a result, inhibitors consume all

the radicals as quickly as they are formed until they, themselves, are used up, whereas the retarders only consume some radicals, letting others get by and initiate chain growth. In another contrast to inhibitors, retarders can also react with the growing polymer chains and be chain terminators. Fragments of retarders can, therefore, be found attached to polymer chains.

Kolthoff and Bovey (*53*) demonstrated the actions of retarders and inhibitors and their effects on reaction rates in the manner shown in Figure 4-1. They also demonstrated that the rate of consumption of the inhibitor is independent of its concentration but dependent on the rate of free-radical generation. Thus the consumption is zero-order.

Quinone is a very efficient inhibitor and its reactions were studied extensively. It was found that quinone can act as a very efficient inhibitor at higher concentrations but, surprisingly enough, only as a retarder at lower concentrations (*54*).

Monophenols, on the other hand, are weak inhibitors. Their efficiency appears to increase with the increase in the number of hydroxyl groups (*55*). The location of one hydroxyl group on the phenyl ring in relationship to another appears to be important. For example, catechol is more effective as an inhibitor than resorcinol (*55*).

Aromatic nitro groups act as strong retarders but not as true inhibitors, their effect being proportional to the number of nitro groups present in the molecule. No inhibition was demonstrated by amides or tertiary bases.

4-5. Effect of Oxygen

Oxygen can play a very interesting and significant role in free-radical polymerizations, although not all the ramifications of these oxygen reactions are as yet understood. It was shown in the case of styrene that oxygen can enter the chain and form a copolymer, in other words, act as a comonomer (*56*),

$$CH_2{=}\underset{\underset{C_6H_5}{|}}{CH} + O_2 \rightarrow \text{-}\left[CH_2{-}\underset{\underset{C_6H_5}{|}}{CH}\right]_n O{-}O\text{-}\left[CH_2{-}\underset{\underset{C_6H_5}{|}}{CH}\right]_m O{-}O\sim$$

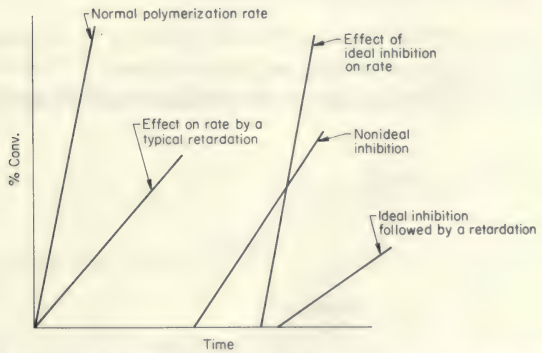
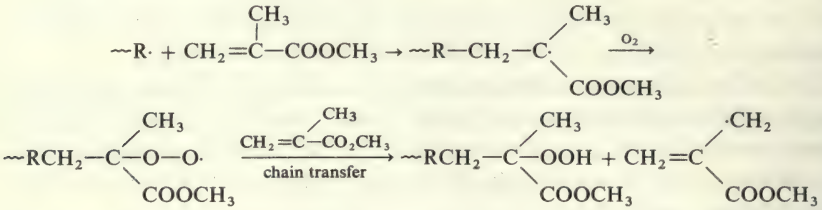


Figure 4-1. Demonstration of effects of inhibitors and retarders.

But, with methyl methacrylate, oxygen was shown instead to form both peroxides and hydroperoxides (*57*),



The above peroxide radical is stable against addition to new monomers (methyl methacrylate). This results in marked retardation exerted by oxygen on the polymerization and also in the formation of hydroperoxides rather than peroxy links, as in the case of styrene. So, as shown, oxygen may influence polymerization in several ways. Furthermore, sometimes it may act as an inhibitor or as a retarder and, at other times, even as a catalyst. This was demonstrated in a number of studies. For instance, it was found that oxygen retards the photopolymerization of vinyl acetate and acrylic acid or its esters, but actually accelerates photopolymerization of styrene; however, in thermal polymerization of styrene, oxygen acts merely as a weak accelerator during the early stages of the reaction but as a retarder during the last stages (*52*).

4-6. Thermal Polymerization

Certain monomers, such as styrene and others that have been carefully purified and freed of all possible initiators, will still polymerize at elevated temperatures. This is believed to be due to thermally induced decomposition of monomers to radicals. The rates for such reactions appear to be smaller than those with chemical initiators (*58*).

4-7. Kinetics of Free-Radical Polymerization

Earlier we separated the polymerization process in its simplest form into three steps: initiation, propagation, and termination.

Actually, the initiation step can be subdivided further, into two more steps (*59*):

1. Formation of the radical:

$$I \xrightarrow{K_d} 2R\cdot$$

2. Formation of the chain radical:

$$R\cdot + M \xrightarrow{K_a} RM\cdot$$

The various steps in propagation can all be expressed as

$$RM\cdot + xM \xrightarrow{K_p} R(M)\cdot_{x+1}$$

It is assumed that each individual step of monomer addition to the growing chain (occurring x times) is equivalent at the rate constant K_p, independent of the chain length.

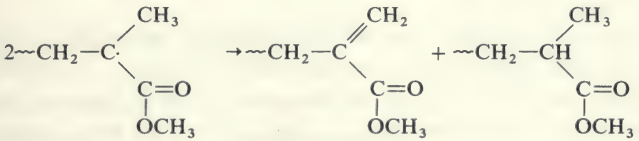
Termination can occur by two mechanisms: combination or coupling of two radical chains,

$$2\sim CH_2CHX\cdot \xrightarrow{K_t} \sim CH_2CHX{-}CHX{-}CH_2\sim$$

or disproportionation through transfering a proton and formation of a terminal olefin,

$$2\sim CH_2CHX\cdot \xrightarrow{K_t} \sim CH_2CH_2X + \sim CH{=}CHX$$

An example of such disproportionation can be shown on methyl methacrylate (*60*),



Poly(methyl methacrylate) was shown (*60*) to disproportionate almost entirely at temperatures above 60°C, and partly by each method below that temperature. Styrene, on the other hand, will usually terminate by combination.

The rate of initiation can be expressed

$$v_i = \left(\frac{d[M\cdot]}{dt}\right)_i = 2fk_d[I] \tag{1}$$

where f is the fraction of radical formed and I represents the amount of initiation used. The rate of termination is

$$v_t = -\left(\frac{d[M\cdot]}{dt}\right)_t = 2k_t[M\cdot]^2 \tag{2}$$

When $v_i = v_t$, a steady state condition prevails.

The rate of propagation is essentially the same as the overall rate of disappearance of monomer,

$$v_p = -\frac{d[M]}{dt} = k_p[M][M\cdot]$$

but (M·) can be solved by combining the initiation and termination equations (1) and (2),

$$[M\cdot] = \left(\frac{fk_d[I]}{k_t}\right)^{1/2}$$

Thus v_p becomes

$$v_p = k_p\left(\frac{f k_d[\mathrm{I}]}{k_t}\right)^{1/2}[\mathrm{M}]$$

Initiator efficiencies can be determined by comparing the amount of initiator decomposed with the number of its fragments that started polymer chains. This can usually be followed with analytical routines (*61*).

If the K_d and K_a are known, the ratio of the rate constants K_p^2/K_t can be evaluated from the overall polymerization rate,

$$\frac{K_p^2}{K_t} = \frac{2v_p^2}{v_i[\mathrm{M}]^2}$$

The overall rate, of course, is a function of conversion. If initiator concentration does not change appreciably during the course of polymerization and initiator efficiency is independent of monomer concentration, then polymerization is said to proceed by first-order kinetics, the rate being proportional to monomer concentration.

In some monomers, such as methyl methacrylate, when the polymerization is being carried out in bulk or in concentrated solution, a marked deviation from first-order kinetics occurs in the direction of an increase in the reaction rate. This phenomenon is referred to as *autoacceleration.* It is accompanied by an increase in molecular weight. Because the effect is independent of initiator, it must be due to a change in K_p^2/K_t. Interestingly enough, this was shown to be dependent upon the viscosity of the polymerization medium and independent of the means by which any increases in viscosity might be created. (Addition of a thickening agent can cause the production of the autocatalytic effect.) The effect is believed to be caused by a decrease in the rate of diffusion of the polymer molecules through the viscous medium, thus lowering the ability of two long-chain radicals to come together and terminate. This reduction of the termination constant due to lack of chain mobility resulting from viscosity increases is known as the *Tramsdorf-Norrish effect* (*62, 63*).

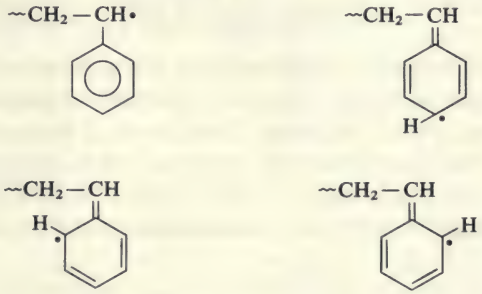
The chain propagation can have four routes:

1. $\sim\mathrm{P}-\mathrm{CH_2}-\mathrm{CXY}\cdot + \mathrm{CH_2}=\mathrm{CXY} \rightarrow \sim\mathrm{PCH_2CXYCH_2CXY}\cdot$
2. $\sim\mathrm{P}-\mathrm{CH_2}-\mathrm{CXY}\cdot + \mathrm{CXY}=\mathrm{CH_2} \rightarrow \sim\mathrm{PCH_2CXYCXY}-\mathrm{CH_2}\cdot$
3. $\sim\mathrm{P}-\mathrm{CXY}-\mathrm{CH_2}\cdot + \mathrm{CXY}=\mathrm{CH_2} \rightarrow \sim\mathrm{PCXY}-\mathrm{CH_2}-\mathrm{CXY}-\mathrm{CH_2}\cdot$
4. $\sim\mathrm{P}-\mathrm{CXYCH_2}\cdot + \mathrm{CH_2}=\mathrm{CXY} \rightarrow \sim\mathrm{PCXYCH_2}-\mathrm{CH_2}-\mathrm{CXY}\cdot$

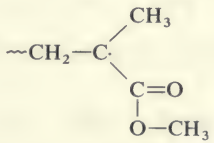
Reaction 1 would lead to chains of regular structure in which the substituents are on alternate carbons. Such a 1,3 structure is referred to as a *head-to-tail structure.* Reactions 2 and 4 lead to alternate additions and are referred to as head-to-head and tail-to-tail additions.

A large amount of evidence exists that 1,3 structures actually predominate in vinyl polymers. This structure apparently arises from reactions 1 and 3. The unpaired electron of the growing radical chain appears associated with the carbon atom carrying the substituent. The effect is particularly noticeable in

olefins substituted with benzene rings. This is true even though a styrene-terminated chain radical can be pictured as assuming four configurations (*64*):



Electron-spin-resonance studies have provided information on the configuration of some growing radicals. Thus poly(methyl methacrylate) radical was shown to be (*65*)



leading to a head-to-tail type of addition.

In chain growth two factors are generally important: reactivity of the radical and reactivity of the monomer. The second depends upon polarity of the double bond and upon steric factors. The polarity is a function of the ability of the substituents to either donate or withdraw electrons.

The order of reactivity of monomers appears to originate in resonance stabilization of the transition states during the addition to growing radical chain. And, of course, the more reactive the monomer, the greater will be the resonance energy of the resultant radical after addition (*66*), thereby making it more stable and less reactive.

4-8. Chain Transfer

The mechanism that explains production of additional molecules during polymerization is that of transfer of activity of one growing chain to some other molecule. The original chain loses its capacity for further growth because it becomes terminated in this process, and the second molecule, called the *transferring agent*, now becomes a free radical capable of adding monomer units and growing into a polymer (*67*).

A very typical case of such transfer is removal by a chain radical of a proton (or some other atom) from another molecule. Another such molecule may be the solvent (and often is), a monomer, an initiator molecule, or another polymer

molecule. In sum, the degree of polymerization may be expressed

$$\bar{X}_n = \sum \frac{\text{rate of growth}}{\text{rates of termination by all processes}}$$

The efficiency of various compounds as chain-transferring agents varies widely with molecular structure. Obviously the ease of proton removal will be an important factor in such reactions. Thus aromatic hydrocarbons are rather unreactive unless they have a benzylic hydrogen. Mercaptans are very efficient chain-transferring agents because of the acidity of sulfhydryl groups. The reaction of chain transferring to, say, cumene can be shown as

The above mechanism is also true for ethyl benzene and other compounds.

With mercaptans it can be shown as follows:

$$\sim\!P\cdot + RSH \rightarrow \sim\!PH + RS\cdot$$

and in the case with disulfides, an abstraction of a sulfide radical can take place in this manner:

$$\sim\!P\cdot + RSSR' \rightarrow \sim\!PSR + R'S\cdot$$

The transfer reaction was observed to be affected by temperature but not by changes in the viscosity of the reacting medium (*61*).

When transfer occurs to a monomer, it appears to be independent of the polymerization rate (*68*). However, when transfer to the initiator occurs, the rate increases rapidly (*69*).

Transfer to monomers can be demonstrated as being of two types:

1. $\sim CH_2-\dot{C}HX\cdot + CH_2=CHX \rightarrow \sim CH_2CH_2X + CH_2=\dot{C}\!\!<_{X}$

or

2. $\sim CH_2-CHX\cdot + \dot{C}H_2=CHX \rightarrow \sim CH=CHX + CH_3-\dot{C}HX$

In cases of chain transferring to polymers, no new molecules are produced but branching is formed. Such transferring can take place from a growing chain to another "dead" polymer, or from the growing chain end to some position on its own backbone. This is commonly referred to as *backbiting*, and it can be illustrated as follows:

The new radical on the polymer backbone now becomes a site for fresh chain growth, which, of course, becomes a branch.

Chain transferring has greater effect on molecular-weight distribution than on molecular weight itself. At the same time, chain-transferring agents with transfer constants near unity are quite useful in depressing molecular weights in polymerization reactions (*70*).

4-9. Copolymerization

Copolymerization of two different monomers can be expected to give the mechanism of reaction a somewhat different character than the one encountered in the formation of homopolymers. Specifically, in propagation, the monomers can add in four different ways (*71*):

1. $\sim\!M_1\cdot + M_1 \xrightarrow{K_{11}} \sim\!M_1M_1\cdot$
2. $\sim\!M_1\cdot + M_2 \xrightarrow{K_{12}} \sim\!M_1M_2\cdot$
3. $\sim\!M_2\cdot + M_1 \xrightarrow{K_{21}} \sim\!M_2M_1\cdot$
4. $\sim\!M_2\cdot + M_2 \xrightarrow{K_{22}} \sim\!M_2M_2\cdot$

The rates of these reactions can be used to define the reactivity ratios of the two monomers:

$$r_1 = \frac{K_{11}}{K_{12}} \qquad \text{and} \qquad r_2 = \frac{K_{22}}{K_{21}}$$

Using these r values, the composition of the copolymers can be found from the copolymerization equation (*72*),

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\left(\frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]}\right)$$

when M_1 and M_2 are concentrations of the two monomers. These reactivity ratios, r_1 and r_2, may be looked upon as ratios of the rate constant for a given radical for adding its own monomer vs. that for adding the other monomer. Thus when $r_1 > 1$, the radical $\sim\!M_1\cdot$ will add monomer M_1 at a faster rate than monomer M_2, but when $r_1 < 1$, the situation is reversed. Some typical reactivity ratios are presented in Table 4-4. [An extensive compilation of reactivity ratios has been made by Young (*73*).]

For an ideal system, $K_{11}/K_{12} = K_{21}/K_{22}$, and $r_1 \times r_2$ should be equal to 1.

Where both r_1 and r_2 are equal to zero, each radical prefers to react with the other monomer and the monomers will alternate with each other, regardless of the composition of monomer feed.

Actually these are almost hypothetical cases. In reality in many cases we have $0 < r_1 \times r_2 < 1$. When each radical prefers to add its own monomer and

TABLE 4-4
Some Reactivity Ratios[a]

Monomer 1	Monomer 2	r_1	r_2
Styrene	Butadiene	0.78	1.39
Styrene	Methyl methacrylate	0.52	0.46
Styrene	Vinyl acetate	55	0.01
Vinyl acetate	Vinyl chloride	0.23	1.68
Methyl acrylate	Vinyl chloride	9.0	0.083

[a] From Reference *73*.

$r_1 \times r_2 > 1$, we should get a mixture of homopolymers together with some copolymers.

Alfrey and Price (*74*) attempted to express the factors of general reactivity and polarity quantitatively,

$$K_{12} = P_1 Q_2 e^{-e_1 e_2}$$

where P_1 is the general reactivity of the radical M_1, Q_2 the reactivity of the monomer M_2, and e_1 and e_2 are proportional to the electrostatic interaction of the permanent charges on the substituents in polarizing the double bond.

One can express the r values in terms of Q and e values:

$$r_1 = \left(\frac{Q_1}{Q_2}\right) e^{-e_1(e_1 - e_2)}$$

$$r_2 = \left(\frac{Q_2}{Q_1}\right) e^{-e_2(e_2 - e_1)}$$

$$r_1 r_2 = e^{-(e_1 - e_2)^2}$$

The Alfrey–Price relationship offers a means for predicting monomer reactivity in copolymerization from two fundamental parameters. These are: Q, a measure of the resonance stability of a monomer in copolymerization, and e, polar factors. Thus for the reaction

$$\sim CH_2-\underset{\displaystyle R_1}{\underset{|}{CH}}\cdot + CH_2=\underset{\displaystyle R_2}{\underset{|}{CH}} \rightarrow \sim CH_2-\underset{\displaystyle R_1}{\underset{|}{CH}}-CH_2-\underset{\displaystyle R_2}{\underset{|}{CH}}\cdot$$

Schwan and Price (*75*) believe that Q is the stabilization conferred on the new radical by M_2 and e represents the change induced by M_1 and M_2 on either of the carbons forming the new carbon-carbon covalent bond in transition.

Charton and Capat (*76*) attempted to investigate the composition of e and Q factors by correlating them with the various Hammett substituent constants through use of the expression

$$e_x = m\sigma_x + C$$

This expression was derived from the Alfrey–Price and Hammett equations. They concluded that the e parameter is a function of both inductive and resonance effects.

So far we have discussed the copolymerization of binary systems. Such systems have been explored at great length, and many r values as well as Q and e values can be found in the literature. Ternary systems, on the other hand, have received less attention. The theoretical relationship was expressed by Alfrey and Goldfinger (*77*), who based it on six reactivity ratios: r_{12}, r_{13}, r_{31}, r_{32}, r_{21}, and r_{23}.

$$\frac{a}{b} = \frac{A[A/(r_{31}r_{21}) + B/(r_{21}r_{32}) + C/(r_{31}r_{23})][A + B/r_{12} + C/r_{13}]}{B[A/(r_{12}r_{31}) + B/(r_{12}r_{32}) + C/(r_{32}r_{13})][B + A/r_{21} + C/r_{23}]}$$

$$\frac{a}{c} = \frac{A[A/(r_{31}r_{21}) + B/(r_{21}r_{32}) + C/(r_{31}r_{23})][A + B/r_{12} + C/r_{13}]}{C[A/(r_{13}r_{21}) + B/(r_{23}r_{12}) + C/(r_{13}r_{23})][C + A/r_{13} + B/r_{32}]}$$

where a, b, and c are the quantities of each monomer found in the resultant terpolymer and A, B, and C are the quantities of the monomer in the feed system. Needless to say, ternary and higher systems become progressively more difficult to treat rigorously.

It might be proper to describe here a picture of the kinetic model for free-radical polymerization of homopolymers or copolymers. Such a model calls for first-order initiator decomposition and second-order polymer propagation and termination reactions. Furthermore, the propagation rate is assumed to be independent of the chain length, with the termination occurring primarily by combination rather than by disproportion. This last assumption also requires that no chain transferring take place with either the solvent or the polymer. Such a kinetic model would also require that all the kinetic constants remain truly constant, regardless of the degree of polymerization.

4-10. Allylic Polymerization

Special mention must be made of polymerizations involving allylic compounds. This is due to the fact that unlike vinyl compounds, polymerization of allylic compounds (by free-radical mechanism) does not lead to high molecular weights but to mixtures of dimers and trimers.

The explanation lies in the fact that allylic monomer radical is resonance-stabilized to the point of failing to propagate chain growth,

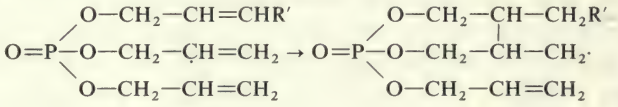
$$CH_2{=}CH\dot{C}HOH \rightleftharpoons \cdot CH_2CH{=}CHOH$$

So, instead of propagation, chain transferring occurs. But such chain transferring will be essentially a terminating reaction (*78*),

$$\sim CH_2{-}\underset{\displaystyle \underset{\displaystyle \underset{H}{O}}{|}\,CH_2}{\overset{|}{C}}H\cdot + CH_2{=}CH{-}CH_2OH \rightarrow \sim CH_2{-}\underset{\displaystyle \underset{\displaystyle \underset{H}{O}}{|}\,CH_2}{\overset{|}{C}}H_2 + CH_2{=}CH\dot{C}HOH$$

As a result, it is often referred to as *degradative* chain transferring.

Polyallyl compounds will polymerize to form a three-dimensional lattice, however, by this chain-transferring process (*78*),



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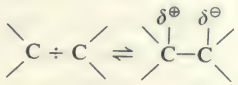
Ionic Polymerization

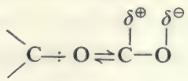
5

5-1. Chemistry of Nonradical Chain Polymerization

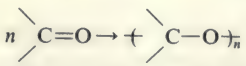
In Chapter 4 the mechanism of free-radical polymerizations was considered. This type of polymerization is limited to monomers possessing carbon-to-carbon double bonds. Their ability to combine into macromolecules by free-radical mechanism depends upon the activity of π-electrons,



Ionic polymerization of olefinic monomers is also dependent upon the activity of π-electrons. But ionic initiators permit a broader choice of monomers. Thus, for instance, carbonyls, which also possess π-electrons, can also be polymerized by ionic mechanism. In the carbonyls the π-electrons are somewhat displaced,



Nevertheless, they are available for polymer formation,



A third functional unit, one which lacks the π-electron but is a strained structure, is a cyclic ether. Here the crowding of the nucleus activates one of the electron pairs on the oxygen atom with the result that ionic initiation can cause ring opening and chain propagation leading to polymers. This third group of monomers susceptible to ionic polymerization includes oxirane rings, oxitanes, furans, and so on.

The mechanism of ionic polymerization can be divided into two general types, depending upon the nature of the carrier ions of the growing polymer chains. When the chains carry a positive ion center, or a carbonium ion, the polymerization is said to proceed by a *cationic* mechanism. When, however, they carry a negative ion or a carbanion, then they are called *anionic.*

Higashimura and co-workers (*1*) compare the two reactions by picturing the cationic polymerization as being initiated by an electrophilic attack of the initiator on the monomer and the anionic polymerization as one being initiated by a nucleophilic attack:

Type of reaction	*Reagent monomer*	*Transition state*
Electrophilic addition	$R^{\oplus} + CH_2{=}\underset{\displaystyle X}{\underset{\vert}{CH}}$	$\rightarrow R{:}CH_2{-}\overset{\displaystyle \oplus}{\underset{\displaystyle X}{\underset{\vert}{CH}}}$
Nucleophilic addition	$R^{\ominus} + CH_2{=}\underset{\displaystyle X}{\underset{\vert}{CH}}$	$\rightarrow R{:}CH_2{-}\overset{\displaystyle \ominus}{\underset{\displaystyle X}{\underset{\vert}{CH}}}$

In general, ionic polymerizations involve initially the dissociation of a particle into a positive and a negative ion in an organic environment. Propagation then occurs through successive additions of monomeric units to the charged or "reactive" ends of the growing chains. This process takes place in a liquid homogeneous system, the motions being fully at random with all segments of the growing chains, including the "reactive" ends. This means that the transition states for each propagation must be formed repeatedly out of the general molecular disorder of the liquid phase.

Such polymerizations carried out in solution are characterized by high rates at the low temperatures that are usually employed for these reactions. The reactivity ratios in copolymerizations are quite different from free-radical ones and actually there are few 1:1 copolymers prepared by ionic mechanism.

The polarity of the double bond is directly related to the susceptibility of the olefins to polymerization. Thus monomers with electron-donating substituents on the double bond can be polymerized cationically, whereas those with electron-withdrawing substituents can be polymerized anionically (*2*).

5-2. Cationic Polymerization

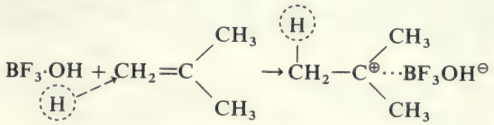
These reactions are facilitated by an electrophilic addition through transferring of a cation, often a proton or a carbonium ion, from the catalyst to the monomer. All Lewis acids are potential catalysts for such reactions. Very often a cocatalyst is involved. Its main purpose is to aid such a transfer. Any convenient source of a cation, such as water or ether, is potentially a useful cocatalyst.

A good illustration of the mechanism of initiation in a cationic polymerization would be the polymerization of isobutylene using a BF_3 catalyst with

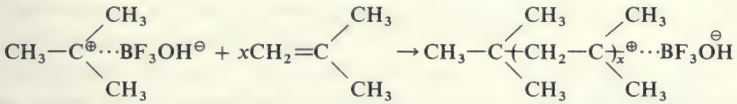
water serving as the cocatalyst. The catalyst-cocatalyst complex species becomes

$$BF_3 + H_2O \rightleftharpoons BF_3{\cdot}OH_2 \rightleftharpoons BF_3OH^{\ominus} \cdots H^{\oplus}$$

When this complex approaches a monomer, transfer of a proton can take place, thereby creating two ionic species,

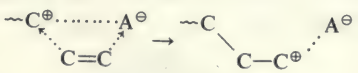


Propagation now proceeds through the mechanism of insertion of the incoming monomer species on the carbonium ion between the charged species,



This scheme shows the counterion as being in the vicinity of the cation center. Such an arrangement is very probable based on energy considerations. This is due to the fact that the reaction usually takes place in a media of relatively low dielectric, so great energy would be required to separate the ion pairs completely. Thus it seems reasonable to assume that the "counterion" remains in close proximity. But, if such is the case, then the nature of this "counterion" becomes very important, because the growing chain remains under the influence of the counteranion complex throughout its growth.

Kennedy (*3*) comments that propagation can best be visualized as a concerted push-pull attack of the carbonium-counterion pair on the monomeric double bond,



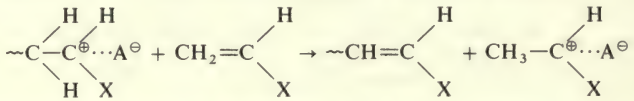
By contrast, as shown in Chapter 4, when a free-radical-initiated polymerization took place, the initiator's function consisted of merely starting chain growth. Once that was accomplished, propagation was independent of the nature of the initiator.

Monomers that can be expected to respond to cationic mechanism should contain groups promoting release of electrons at the double bond. And the initiator, of course, should be a molecule with a strong affinity for coordinating a pair of electrons. The efficiency of the catalyst will be a function of the acid strength of the catalyst-cocatalyst complex. Evans and Polanyi (*4*) found that in polymerization of isobutylene at $-780°C$, the activity of the catalyst decreased in the following order:

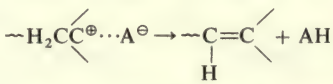
$$BF_3 > AlBr_3 > TiBr_4 > BBr_3 > SnCl_4$$

The reaction time ranged from a few seconds in the case of BF_3 to several days with $SnCl_4$.

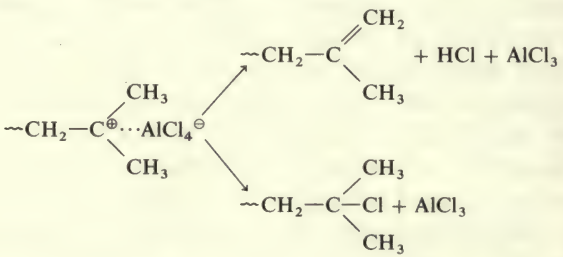
The termination reaction involves abstraction of a proton by the "counterion" or through chain transfer to another monomer. This is due to the fact that when a monomer is placed within the radius of influence of the terminal carbonium ion two competing reactions are possible: either further propagation or a proton abstraction, with the creation of a new growing center,



The mechanism of proton abstraction by the "counterion" is less clear. It is often explained as a unimolecular process,



Thus, in polymerization of isobutene with an aluminum chloride catalyst, the following picture is often shown (*3*):



Neither one of the above terminations would really stop the kinetic chain.

The mechanism of cationic polymerization may be summarized by presenting the following overall scheme:

Initiation:

$$A + RH \rightleftharpoons A{-}RH$$

$$A{-}RH + M \rightarrow HM^{\oplus}\cdots AR^{\ominus}$$

Propagation:

$$HM^{\oplus}\cdots AR^{\ominus} + xM \rightarrow H(M)^{\oplus}_{x+1}\cdots AR^{\ominus}$$

Termination:

$$HM^{\oplus}_{x+1}\cdots AR^{\ominus} \rightarrow M_{x+1} + A{-}RH$$

Chain transfer:

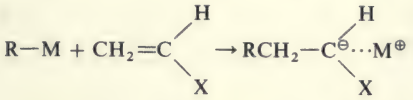
$$HM^{\oplus}_{x+1}\cdots AR^{\ominus} + M \rightarrow M_{x+1} + HM^{\oplus}\cdots AR^{\ominus}$$

It has been found (*5*) that the rate of reaction as well as degree of polymerization are increased by increasing the dielectric constant of the solvent. That is to say, generally propagation rates appear to be reduced by increasing the dielectric constant of the solvent, but this apparently is offset by a reduction in the termination rate with resultant increase in the degree of polymerization.

5-3. Anionic Polymerization

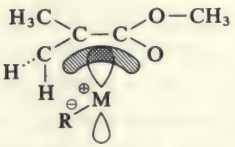
Anionic polymerization, being the chemical counterpart of cationic polymerization, should take place in the presence of catalysts capable of generating carbanions. Metal alkyls and Grignard reagents, as well as dispersions of alkali metals or metal hydrides and amides, fall into this category.

The initiating step can be pictured as the reaction between catalyst and monomers. A metal alkyl can serve as an example of the catalyst,

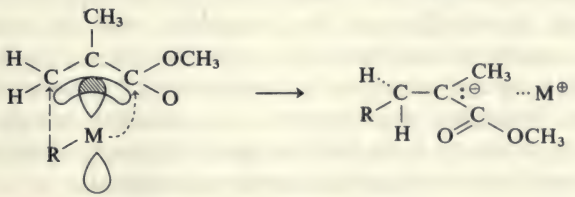


The metal here is the counterion; similar considerations apply to its actions and effects on the polymerization process, as do the counterions in the mechanism of cationic polymerizations.

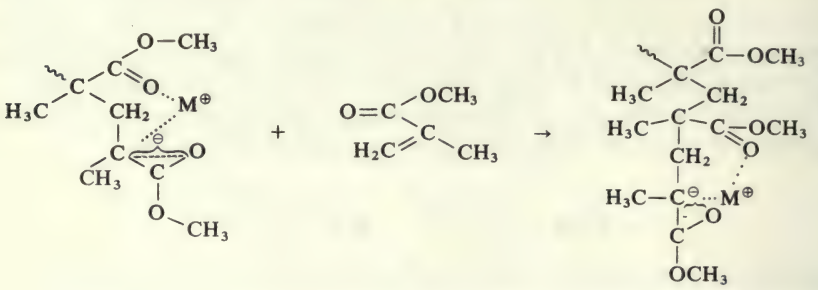
The properties of metal alkyls are consistent with the idea that the metal-carbon bond is an intermediate between being covalent, although highly polarized in the direction $M^{\delta\oplus} \rightarrow R^{\delta\ominus}$, and being fully ionized $M^{\oplus} + R^{\ominus}$. The extent of this in each organometallic species will vary with the nature of the metal and the organic portion. Generally the polymer anion could be regarded as a free propagating species. The driving force for any propagation that might take place would be the initial formation of a complex or coordination between the metal in the covalent and intimate ion-pair form and the π-electron system of the olefinic link of the monomer. After coordination of the olefin has occurred, it will be followed by an intramolecular rearrangement involving migration of the carbanion ($R^{\ominus}$) to the most electrophilic carbon atom of the unsaturated molecule. For example, if the monomer is methyl methacrylate, then we can demonstrate it in this manner:



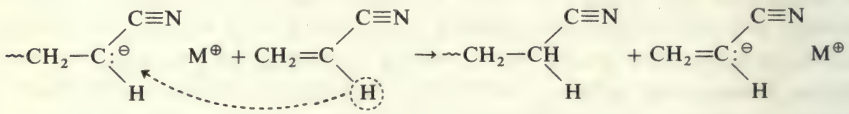
The above picture shows an overlap of the metal bond orbital with the π-electron cloud of the monomer. This overlap causes stretching and eventual rupture of the R—M bond with formation of the carbon–carbon covalent bond and regeneration of a new polar metal–carbon linkage,



The propagation is pictured as actually proceeding by the same mechanism (*6*),



The termination mechanism in anionic polymerization is still not completely clear. Some speculation existed at first on the possibility of hydronium ion transfer (*7*), but energy considerations appear to rule that out. Ottolenghi and Zilkha (*8*) believe that at least in acrylonitrile polymerization it is possible that a transfer occurs from the monomer to the growing chain during termination, simultaneously causing a termination and an initiation of a new active center,



Thus the terminal unit in the resultant polymer will be fully saturated, although the initiating unit will possess an olefinic link.

The overall mechanism of anionic polymerization was summarized by Woodling and Higginson (*9*),

$$CA \rightleftharpoons C^{\oplus} + A^{\ominus}$$

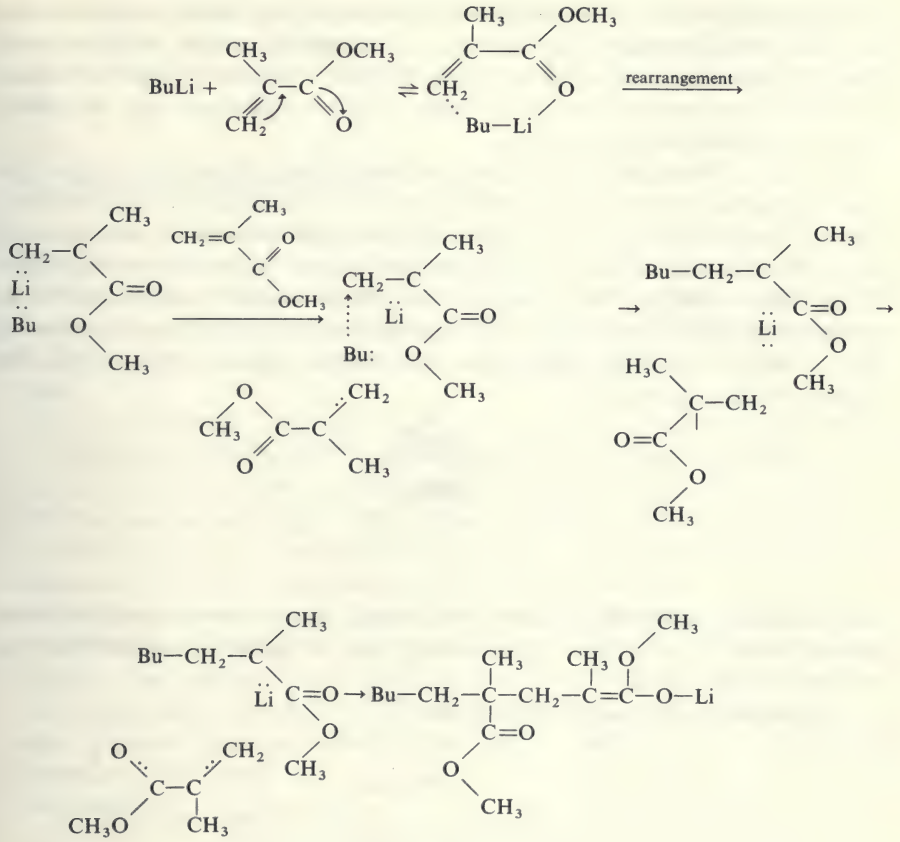
$$A^{\ominus} + M \rightarrow A{-}M^{\ominus}$$

$$A{-}M^{\ominus} + xM \rightarrow A{-}M^{\ominus}_{(x+1)}$$

$$A{-}M^{\ominus}_{(x+1)} + HA \rightarrow A{-}M_{(x+1)}{-}H + A^{\ominus}$$

It is assumed that the presence of a counterion near the charged carbon atom of the terminal unit modifies the electronic configuration of this carbon in such a way that it becomes an sp^3 (tetrahedral) hybrid.

Korotkov and co-workers (*10*) studied the polymerization of methyl methacrylate initiated by butyllithium. They suggested that with butyllithium the chain creation consists of two successive stages: (1) formation of the associate from the butyllithium and monomer molecules, and (2) its isomerization in the direction of the formation of a complex. This complex, which has a linear structure because of the *sp* hybridization, probably reacts with the monomer, forming new complexes of planar structure (an *sp* hybrid),



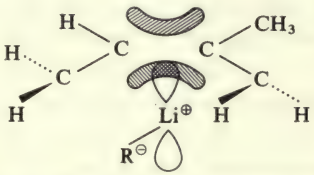
Chain termination is shown as taking place as a result of (1) isomerization of the linear complex with formation of lithium alcoholate, or (2) during interaction with the C=O bond (*10*).

Stille comments (*11*) that not all mechanisms by anionic catalyses are probably exactly alike. This is based on the observation that different monomers respond differently to various anionic initiators. Thus sodium in liquid ammonia is capable of polymerizing various acrylic monomers but incapable of polymerizing butadiene and forms only low polymers from styrene. On the other hand, these two monomers polymerize readily in the presence of sodium dispersions. In addition, the steric controls that can be achieved with diene polymerizations using certain metal alkyls differ with the choice of solvents (*12–14*).

O'Driscoll and Tobolsky (*15*) demonstrated that the rate of polymerization of styrene using butyllithium as the catalyst is independent of the catalyst concentration over a hundredfold range with benzene as the solvent. In tetrahydrofuran, on the other hand, the rate is proportional to the catalyst concentration.

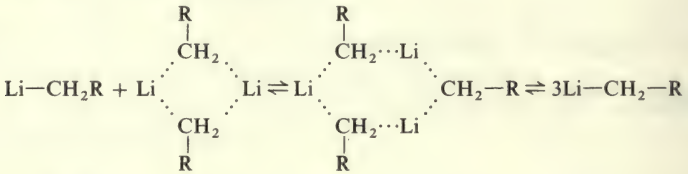
The explanation for the above phenomenon can be found in the fact that butyllithium is associated in benzene as a hexameric species, with the result that unimolecular concentration is low. On the other hand, tetrahydrofuran complexes the butyllithium and causes it to be dissociated into tetramers, dimers, and individual molecules.

Lithium- or butyllithium-catalyzed polymerizations of dienes are largely the result of stepwise growths of essentially covalent, or intimate ion-pair, lithium–carbon bonds. If one chooses to accept the analogy between the interaction of an acrylate monomer and alkyllithium and that of isoprene and a covalent alkyllithium molecule, then a very similar picture can be drawn for the diene to represent the initiation step in a manner similar to that shown earlier for methyl methacrylate polymerization. An electron cloud overlaps with the lithium electron as follows:

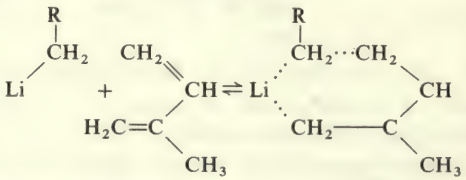


One can also explain the formation of the high *cis*-1,4 content of polyisoprenes formed with Li initiation by assuming that a pseudo-six-membered-ring intermediate is formed.

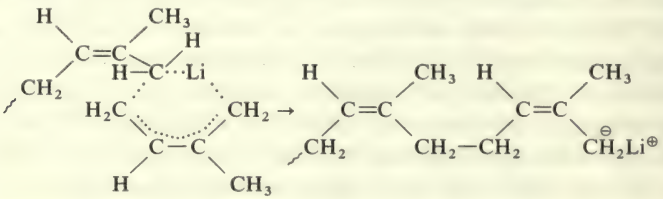
1. Lithium alkyl trimer dissociates first:



2. Then alkyllithium is added to isoprene:



3. Propagation then proceeds as follows:



The above mechanism would be particularly favored for lithium alkyls (as compared to other organometallic compounds) because of the small ionic radius of lithium and the high proportion of *p*-character of its outermost orbital.

5-4. Polymerization of Carbonyls

Formaldehyde Polymerization

Addition polymerizations of formaldehyde can lead to high-molecular-weight products. These reactions are possible with or without the presence of inert diluents. The mechanism may be cationic or anionic; the first one requires relatively strong acids, whereas the second one requires only the use of weak bases.

The conventional procedure (*16*) for attaining high-molecular-weight products calls for highly purified monomers to eliminate transfer agents.

A hydrocarbon solvent may be used at temperatures between 25 and 75°C, with the gaseous monomer being added continuously. Conditions must be such that an initiator is present which is active enough to maintain low concentration of dissolved formaldehyde during polymerization.

Many Lewis acids are good cationic initiators for forming a high-molecular-weight product. Other strong electrophilic agents may be used as well. Good examples of satisfactory Lewis acid catalysts are Al, Br_3, and $FeBr_3$.

Tertiary amines represent good anionic initiators. A cocatalyst, such as water or alcohol, may be required. The anionic mechanism of the reaction is pictured as follows (*16*):

Initiation:

$$R_3NH^{\oplus}OH^{\ominus} + CH_2{=}O \rightarrow HOCH_2O^{\ominus}R_3NH^{\oplus}$$

Propagation:

$$HO(CH_2O)_nCH_2O^{\ominus}R_3NH^{\oplus} + CH_2O \rightarrow HO(CH_2O)_{n+1}CH_2\overset{\ominus}{O}R_3\overset{\oplus}{N}H$$

Transfer:

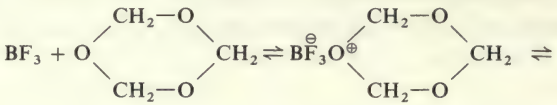
$$HO(CH_2O)_{n+1}CH_2O^{\ominus}R_3NH^{\oplus} + R'OH \rightarrow HO(CH_2O)_{n+1}CH_2OH + R_3N\overset{\oplus}{H}O\overset{\ominus}{R'}$$

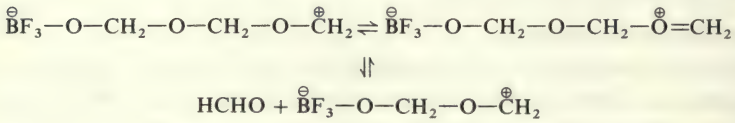
Reinitiation:

$$R_3N\overset{\oplus}{H}O\overset{\ominus}{R'} + CH_2O \rightarrow R'OCH_2O^{\ominus} + R_3NH^{\oplus}$$

In place of monomeric formaldehyde, trioxane, which is polymerized by cationic mechanism, may be used (*17*, *18*). The reaction mechanism is believed to involve direct coordination of the Lewis acid (BF_3 or others) with the oxygen in the trioxane molecule. This results in a ring opening that is induced in order

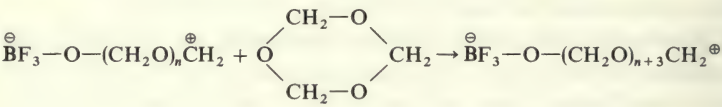
to form a resonance-stabilized zwitterion:





Equilibrium is established between formaldehyde and reactive polyoxymethylene oligomer. This leads to formation of a low-molecular-weight polymer which forms a low-molecular-weight nucleus. From the surface of this nucleus polymerization then proceeds rapidly.

The propagation (*17*, *18*) was as shown below, (the termination step has not been explained, as yet):

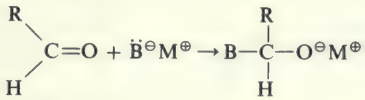


Polymerization of Higher Aldehydes

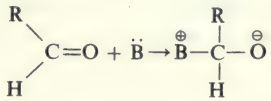
Vogl, who studied catalytic polymerization of aldehydes (*19–24*), concluded that polymerization of aldehydes fits well into the definition of ionic polymerizations (*21*). He points to the fact that not only can aldehydes be polymerized by both anionic and cationic mechanisms, but stereospecific polymers can be obtained by both mechanisms. Vogl further noted a possible correlation between polarization of the C=O bond, as observed by infrared spectroscopy, and its polymerizability. Thus aldehydes which possess the characteristic carbonyl absorption at 1750 cm^{-1} (such as chloral and formaldehyde) will polymerize readily with such weak nucleophiles as pyridine. Saturated aldehydes with carbonyl absorption at 1750–1725 cm^{-1} can be polymerized by utilizing alkali alkoxides, alkyls, and Grignard reagents, whereas special methods are required to polymerize carbonyl compounds with a frequency of less than 1725 cm^{-1}. This decrease in carbonyl frequency apparently parallels an increase in the electron density at the carbonyl carbon, which tends to hinder polymerization of carbonyl double bond (acrolen, acetone).

Most aldehyde polymerizations proceed well at low temperatures, such as −78°C, with a low-dielectric solvent yielding the best results. The polymerization can again be subdivided into initiation, propagation, and termination (or transfer).

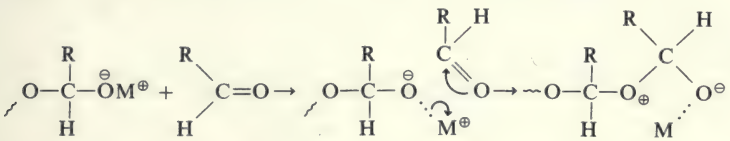
Vogl and Bryant (*24*) picture anionic initiation as the addition of nucleophiles to the carbonyl carbon with placement of the cationic counterion at the carbonyl oxygen,



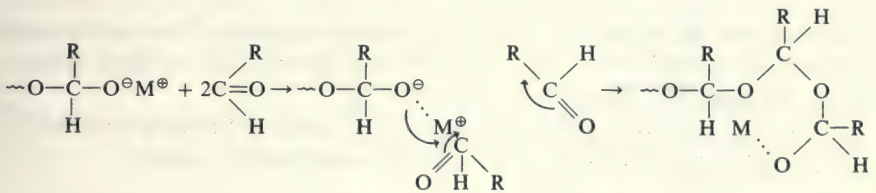
If the initiator is pyridine, then initiation can be pictured in this manner:



Anionic propagation, as a first approximation, can be pictured as involving a four-center intermediate,



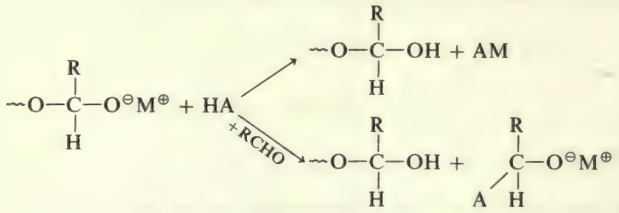
Stereoregular polyaldehydes always precipitate during polymerization. This results in less than half of the monomer being in solution and the rest being adsorbed on the polymer chain, with the metal cations most likely tetracoordinating rather than dicoordinating under these conditions. This leads Vogl and Bryant (*24*) to propose an alternative anionic mechanism, based on the idea that more than one monomer unit is involved in the transition state of propagation:



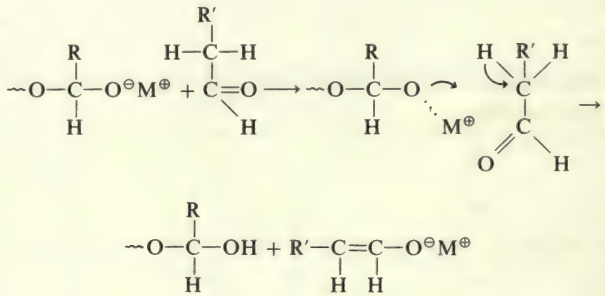
The fourth coordination is satisfied with an ether oxygen of the growing polymer chain. Vogl and Bryant believe that this "next neighbor" is probably the oxygen of the penultimate unit, but that the metal ion could also coordinate with the oxygen, one unit further back in the chain.

Chain transfer during aldehyde polymerization could arise by (1) proton transfer from a chain-transferring agent, (2) proton transfer from monomer, or (3) hydride transfer to monomer.

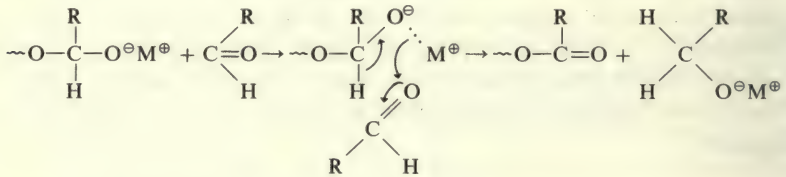
Thus case (1) can be represented as



The aldehyde hydrate or hemiacetal is capable of functioning as a chain terminator (*24*). Case (2) can be shown as

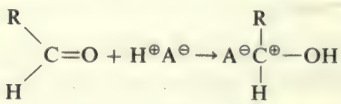


So far, chain transfer with a monomer has not been demonstrated. Case (3) based on the hydride transfer can be illustrated as follows:



The cationic initiators can be separated into three groups. These were studied by several investigators (*22–24*), by Letort and Mathis (*25*), and by Furukawa and co-workers (*26*). The three groups are:

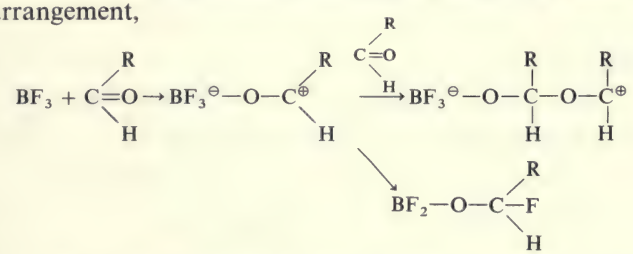
1. Protonic acids that will add across double bonds of the carbonyls, leaving one hydroxyl end group and a growing carbonium ion per adduct,



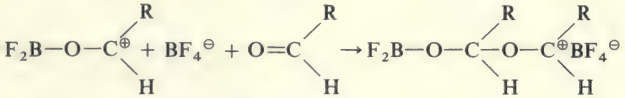
The initiation should be influenced only by the capability of the acid to protonate the carbonyl oxygen. Propagation would require only a low degree of nucleophilicity to avoid termination by recombination with the carbonium ion.

2. Alkylation or acylation of the carbonyl oxygen by stable carbonium ions (*27–33*).

3. Lewis acids. Letort and Mathis (*25*) and Furukawa et al. (*26*) explain this mechanism by drawing an analogy to cationic polymerizations of styrene. Kern et al. (*31*) disagree, however, and offer an alternative mechanism which involves addition of the Lewis acid to carbonyl, followed by either polymerization or rearrangement,



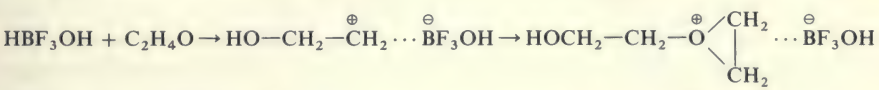
The product from rearrangement can presumably add another mole of the Lewis acid to form a carbonium ion which could initiate chain growth,



The mechanism for termination in these polymerizations is not clear, although chain transferring may be plausible in some cases.

5-5. Polymerization of Oxyranes

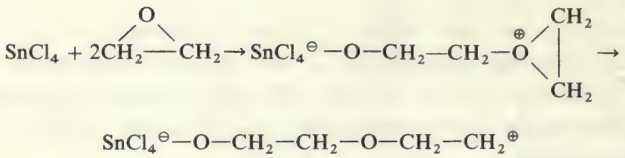
The conversion of epoxides to high-molecular-weight polyethers can be accomplished in a variety of ways. Both cationic and anionic catalysis is possible. Lewis acids such as BF_3 or $SnCl_4$ usually lead to low-molecular-weight products. Thus, if BF_3 is used, a reversible chain transfer occurs (*34*). The catalyst is not consumed and the growth stops at a low molecular weight, owing to dimer formation.



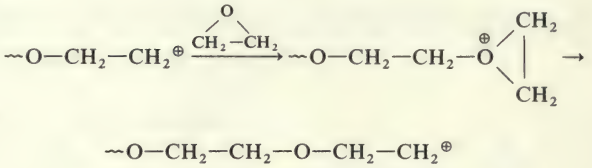
As one might guess, a small amount of water is required as a cocatalyst for the above reaction. Each polymer molecule has one hydroxy end group. Dimer formation was also shown to occur, through catalyst-induced decomposition of the polymer chain (*35*).

The polymerization reaction catalyzed by stannic chloride is different in that water is not needed for the reaction to take place (*36*). Two polymer molecules can form for each molecule of the catalyst. Chain termination involves catalyst destruction rather than transfer:

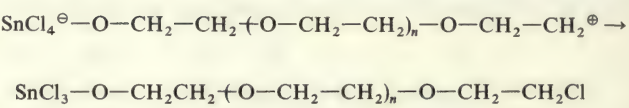
Initiation:



Propagation:

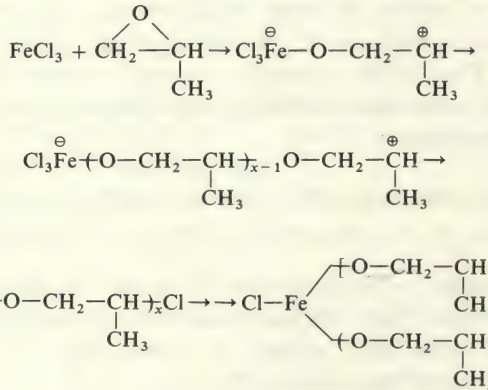


Termination:



Ferric chloride forms a red catalyst oil with propylene oxide and also yields an isotactic polymer from this monomer (*37–39*). This catalyst will polymerize *l*-propylene oxide to an optically active polymer.

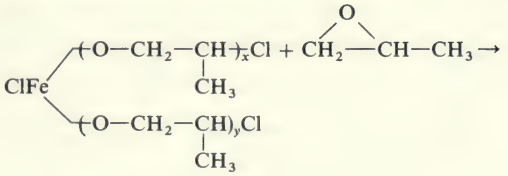
Colclough and co-workers (*40*) claim that this catalyst goes through several consecutive addition steps with the epoxide. This occurs on at least two different halogen sites before migration to carbon takes place,

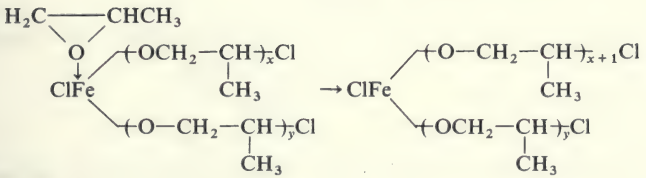


catalyst

After the catalyst is formed, it inserts the incoming monomer molecules between the metal and oxygen bond (*40–42*):

Propagation:

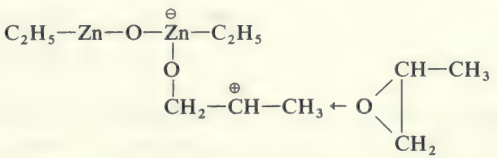




Diethyl zinc–water is one of the more effective catalysts for polymerization of propylene oxide, leading to high polymer formation. This was originally investigated by Furukawa and co-workers (*43*) and Chu and Price (*44*). Bailey and France (*45*) and Gorty and co-workers (*46*) investigated dibutyl zinc with several cocatalysts.

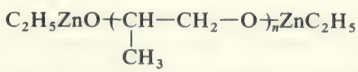
Booth et al. (*47*) used dioxane solvent for polymerization of propylene oxide catalyzed by diethyl zinc–water. They felt that their results indicated a similarity to polymerizations of propylene oxide by ferric chloride–water (*48*) and by aluminum triethyl–water, studied by Colclough and Wilkinson (*49*), who proposed a mechanism based on cationically active centers. Several paths were shown for the reaction; assuming that $C_2H_5ZnOZnC_2H_5$ is the important catalyst species, then initially what takes place is:

1. Solvation of cation with monomer:



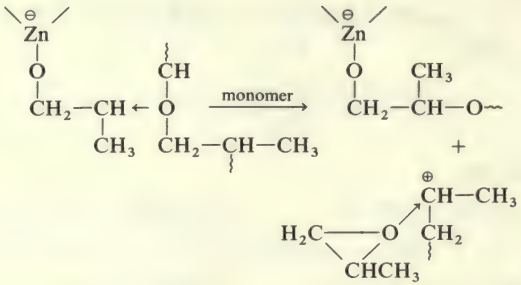
2. Solvation with an oxygen in the polymer chain (which they feel must occur preferentially at a point removed from the cation by four monomer units), leading to cyclization.

3. Reaction with an oxygen in the counterion, which gives the species



where n denotes a small polymer chain. This species will probably associate into large complexes and be relatively inactive (*49*). Such a reaction can be the cause of a rapid decrease in the rate of the initial reaction.

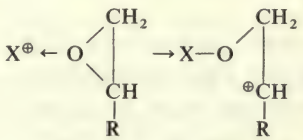
4. Solvation with an oxygen in a second polymer chain leading to a scission reaction:



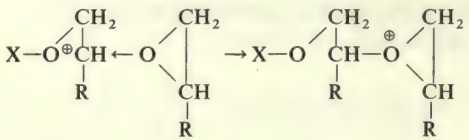
This proposed mechanism is at odds with a coordinate anionic mechanism originally proposed by Price and Osgen (*38*).

Bruce and Hurst (*51*) suggest a cationic-active-center mechanism instead.

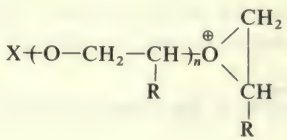
By representing the cationic site on the catalyst as $X^{\oplus}$, the coordination of the monomer followed by a ring opening to a carbonium ion is shown as follows:



A further monomer then becomes associated, yielding a hybrid,



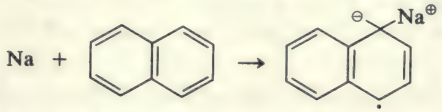
This is also possible by way of a ring opening aided by the second monomer molecule. Repetition of the process leads to polymer formation,



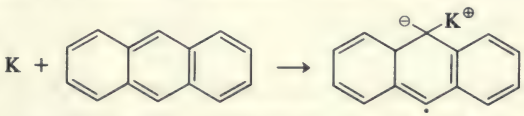
Either process would require an electron transfer from the monomer and/or stabilization of a secondary carbonium ion by the group R. This would make the expected rates to be in the order of R = phenyl; *t*-butyl > *t*-butyl CH_2 > ethyl > methyl > H. Actually, the reverse was observed. This discrepancy was explained on the basis of steric factors (*51*).

5-6. Radical Anion Polymerization

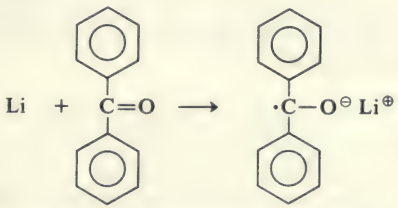
Alkali metals such as lithium, sodium, and potassium will produce colored solutions with certain aromatic hydrocarbons. Sodium, for instance, was shown to form an ion-radical couple with naphthalene in tetrahydrofuran,



Potassium was shown to undergo a similar reaction with anthracene,

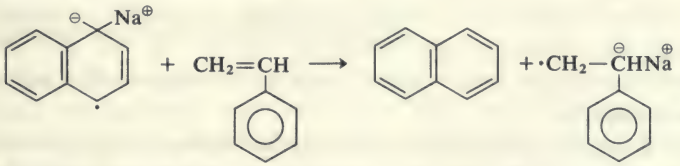


and lithium with benzophenone,

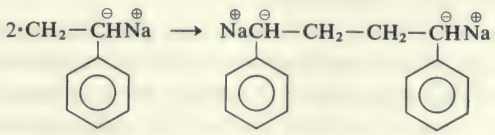


Szwarc and co-workers demonstrated (*52–56*) that styrene polymerizes readily when initiated by a sodium-aromatic hydrocarbon couple, with the molecular weight of the resultant polymer being dependent upon catalyst concentration. The system was demonstrated by Szwarc et al. to be capable of continued chain growth without termination except through quenching. He termed these systems "living" polymers. Addition of comonomers leads to block copolymers.

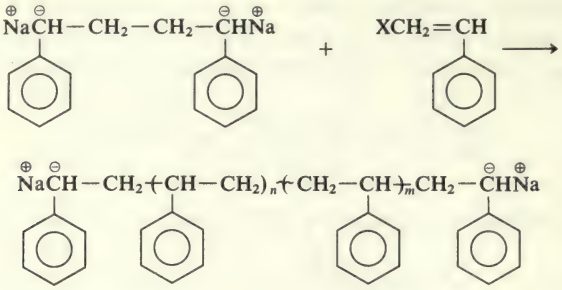
It is generally agreed that the mechanism of initiation involves an electron transfer. This initiation step is a process of actually transferring both the electron and the ion charge to the monomer from the hydrocarbon, with the alkali metal becoming the counterion,



The initiation step is apparently not complete until dimerization of radicals takes place,



Propagation now proceeds at two ends of the chain by the anionic mechanism



Termination is dependent, as mentioned, upon quenching through addition of water, acid, and so on. α-Methyl styrene was shown to be polymerizable by the same system (*57*). Overberger and co-workers (*58*) studied polymerization of methacrylonitrile with lithium and liquid ammonia. Here, too, an electron-transfer mechanism was visualized:

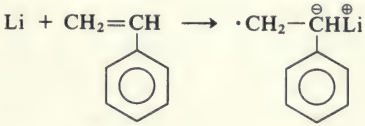
$$Li + 2NH_3 \rightarrow Li^{\oplus}(NH_3) + e\overset{\ominus}{N}H_3$$

$$e\overset{\ominus}{N}H_3 + CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}C{\equiv}N \rightarrow \overset{\ominus}{C}H_2{-}\overset{CH_3}{\overset{|}{C}}{-}C{\equiv}N + NH_3$$

$$2\overset{\ominus}{C}H_2{-}\overset{CH_3}{\overset{|}{C}}{-}C{\equiv}N \rightarrow \overset{\ominus}{C}H_2{-}\overset{CH_3}{\overset{|}{C}}{-}\overset{CH_3}{\overset{|}{C}}{-}\overset{\ominus}{C}H_2$$
$$\qquad\qquad\qquad

mechanisms. Because methyl methacrylate anions are incapable of initiating styrene polymerization (*67*), an anionic mechanism would lead to exclusive poly(methyl methacrylate) species, and because they observed that both monomers were incorporated in the resultant copolymers, they suggested that simultaneous ion and radical growth might be taking place here as well.

In a reinvestigation of these reactions, George and Tobolsky (*68*) reconfirmed the earlier findings, indicating in addition that when lithium metal is used to initiate polymerizations, the initiation takes place by transferring an electron to a monomer to create a radical ion,



This species is also capable of simultaneous radical and anionic growth, and will allow the addition of both styrene and methyl methacrylate to the growing chains (*69*).

Bhattacharyya and co-workers (*70*) pointed out that lack of termination in "living" anionic polymerizations permits one to determine directly the absolute rate constants for anionic copolymerizations. They concluded that their results demonstrate that the rate of addition in the case of styrene to an α-methyl styrene ion depends on the counterion and on the structure of the polymer. In particular it depends on the nature of the penultimate unit, the type of linkage between the last unit and the penultimate units, and the size of polymeric molecule.

They also found that polymers grow more slowly when associated with $Cs^{\oplus}$ than with $K^{\oplus}$ counterions. This trend was originally observed for homopolymerization of styrene by Smid and Szwarc (*71*), the rate decreasing along the series

$$Li^{\oplus} > Na^{\oplus} > K^{\oplus} > Cs^{\oplus}$$

In copolymerization, however, this trend apparently is not very clear cut.

5-7. Copolymerization by Ionic Mechanism

Ionic copolymerization can, of course, also be separated into both cationic and anionic mechanisms. But generally, ionic copolymerizations are not handled as simply as free-radical initiated ones because one cannot rely upon reactivity of monomeric species alone. One must also account for activity of the counterion and effect of solvent, which can often exert an influence on the catalyst. Certainly the r values derived for free-radical-initiated copolymerizations no longer apply when an ionic mechanism is employed. This was originally predicted by Mayo and Lewis (*72*) and amply verified by numerous investigations (*73,74*). Nor can one rely upon the Alfrey–Price Q and e values, for here they only tell part of the story.

Cationic copolymerization is therefore a function of the monomer reactivity toward the carbonium ion, the nature of the "counterion," the polarity of the medium, and the reaction temperature. Kennedy points out (*3*) that the overall reactivity of olefinic monomers toward carbonium ions increases by substitution on α-carbon as follows:

$$p\text{CH}_2\text{OC}_6\text{H}_4- > p\text{RC}_6\text{H}_4- > \begin{matrix}\text{C}_6\text{H}_5-\\ \text{CH}_3-\end{matrix} > (\text{CH}_3)_2= >$$

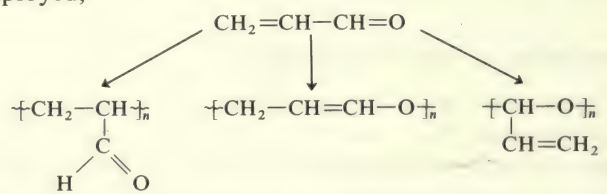
$$\text{C}_6\text{H}_5- > \text{CH}_2=\underset{\displaystyle\text{CH}_3}{\overset{\displaystyle|}{\text{C}}}- > p\text{XC}_6\text{H}_5- > \text{ROOC}-$$

The carbonium ion itself will preferentially attack the carbon atom on the olefinic monomer with the greatest electron density. Thus any electron-donating group will promote reactivity, whereas electron-withdrawing ones will retard such reactivity.

Anionic copolymerization is also strongly influenced by the fact that carbanions rarely exist as free dissociated ions and are usually bound as ion pairs. As a result, steric effects and solvent polarity play a major role in these reactions. Complications can arise in polar solvents from self-termination reactions, isomerization, and reactions with solvents.

Probably the most intriguing aspect of ionic copolymerization is the fact that it allows formation of copolymers of olefins with carbonyls or with ring structures, such as oxyranes or oxytanes, and so on. Much of this work is still in the early stages of exploration. Copolymerization of carbonyls with each other, such as aldehydes, however, has already received some attention. Thus Mark and Ogata (*75*) showed that one can prepare copolymers of formaldehyde and acetaldehyde by both cationic and anionic mechanisms.

Schulz and Passman (*76*) studied polymerization of acrolein with both anionic sodium naphthalene and cationic initiators (BF_3-etherate). Acrolein is an olefinic monomer in a free-radical polymerization, but potentially polymerizable through either the olefin or the carbonyl group when ionic mechanism is employed,



As a result, polymers were formed (*76*) that had only about 2 mole % free aldehyde groups but 70 mole % double bonds.

Noro et al. (*77*) carried out a series of anionic copolymerizations of an aldehyde with vinyl or diene monomers. Thus formaldehyde was block-copolymerized with styrene, α-methyl styrene, 2-methyl-5-vinylpyridine, butadiene, and isoprene, using sodium naphthalene catalysts. The polymerization appeared

to have been initiated by addition of formaldehyde to sodium naphthalene, forming an alcoholate anion, which then was capable of polymerizing formaldehyde to high-molecular-weight polymer (*77*).

Thomas and co-workers (*78*) studied anionic polymerizations of five different alkyl vinyl ketones. The lithium polymerization of isopropyl vinyl ketone appears to have led to some polymers with linkages in the chains other than those expected from a 1,2 type of addition polymerization. So, effectively, the product was a copolymer.

Another interesting copolymer of formaldehyde and carbon monoxide was formed with the aid of Lewis acids by Rogazzini and co-workers (*79*). They found that by using equimolar quantities of formaldehyde and carbon monoxide, a copolymer with the sequences

$$+\overset{O}{\overset{\|}{C}}-CH_2-O+_n \quad \text{and} \quad +\overset{O}{\overset{\|}{C}}-CH_2-O-CH_2-\overset{O}{\overset{\|}{C}}-O+_n$$

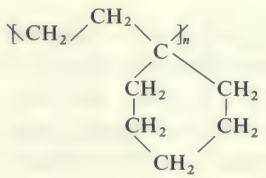
may be formed.

Saegusa et al. (*80*) carried out copolymerizations of cyclic ethers with alkylaluminum catalysts. The monomers were 3,3-bis(chloromethyl) oxacyclobutane, tetrahydrofuran, and epichlorohydrin. Although copolymers were formed in all cases, in the epichlorohydrin and tetrahydrofuran copolymerization considerable amounts of epichlorohydrin homopolymer formed as well.

5-8. Intramolecular Hydride-Shift Polymerization

Kennedy and co-workers reported (*81, 82*) cationic polymerizations of certain olefins in which the propagation steps were apparently accompanied by hydride-shift isomerizations.

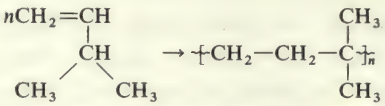
Thus, when vinylcyclohexane was polymerized with the aid of $AlCl_3$ at temperatures ranging from -144 to $+70°C$, a polymer formed in which the repeating units were predominantly



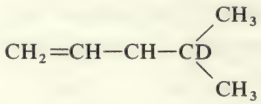
A similar reaction was observed with 3-methyl-butene-1. The initially formed carbonium ion $CH_2-\overset{\oplus}{C}H-CH(CH_3)_2$ apparently rearranges under the influence of strong Lewis acids to the more stable tertiary carbonium ion

$$CH_2-CH_2-\overset{\oplus}{C}-(CH_3)_2$$

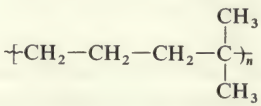
before propagation takes place. The polymer is then made up of repeating units of 2,2′-dimethyl propane



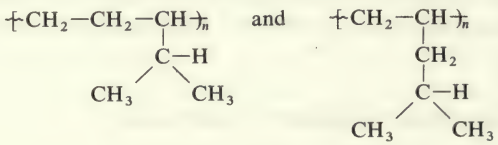
Wanless and Kennedy (*82*) demonstrated this type of rearrangement in the presence of strong Lewis acids with the aid of deuterated 4-methyl-1-pentene,



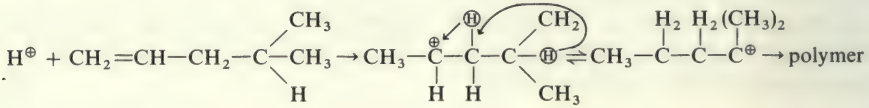
The product consisted mainly of repeating units,



with considerable amounts of the following two structures also present:



In this last case, Wanless and Kennedy feel that successive hydride shifts took place,

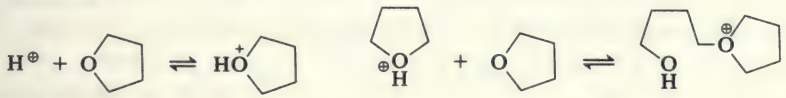


In still another study, Kennedy and co-workers (*83*) investigated the effect of temperature and monomer concentration on the structure and molecular weight of poly(3-methylbutene-1). They observed that structure composition, as determined in terms of the ratio 1,3 units to that of the 1,2 units in the macromolecule, changed with the reaction temperature. Upon lowering the temperatures, the amount of 1,3 increased rapidly and an essentially pure crystalline 1,3-poly-methylbutene-1 was obtained at $-130°C$. The counterion affected strongly the slope of the product composition curve, but the polarity of the medium did not, nor did the monomer concentration or monomer conversion. A reaction mechanism based on a concept of competition between propagation to form 1,2 enchainment and intramolecular hydride shift to form 1,3 enchainment was proposed (*83*).

5-9. Polymerization of Tetrahydrofuran

Tetrahydrofuran is rather unique among the cyclic monomers in that in the polymerization of small-ring monomers, such as ethylene or propylene oxides, the crowding of electrons arising from internal strains leads to the formation of macromolecules. Larger rings, such as tetrahydrofuran, should possess stable conformations and, therefore, should not readily polymerize.

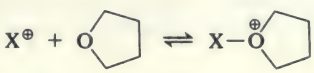
Nevertheless, tetrahydrofuran was first polymerized by Meerwein et al. (*84*) with the aid of strong electrophiles as catalysts and conditions in which the counterion was a poor nucleophile. He used fluorosulfonic and tetrafluoroboric acids, which functioned by means of a secondary oxionium ion,



Meerwein also investigated one Lewis acid, $SbCl_5$, which alone and in low concentrations was capable of initiating tetrahydrofuran polymerizations. Later, phosphorus pentafluoride (*85*) and boron trifluoride (*86*) were also shown to be very efficient Lewis acids for THF polymerization. Thus its polymerization with PF_5 led to a very high molecular weight polymer at 30°C.

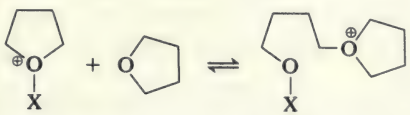
Burrows (*87*) and Bawn et al. (*88*) also explain the mechanism of tetrahydrofuran polymerization, by postulating a strongly electrophilic cation $X^{\oplus}$ on the basis of its forming an oxonium ion as shown above.

Initiation:

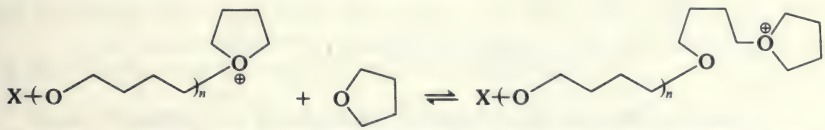


where $X^{\oplus}$ can be $H^{\oplus}$ or another strong electrophile.

This species, although more stable than the carbonium ion, is believed to be sufficiently reactive so that nucleophilic attack by the ether oxygen of the free monomer on the α-carbon of the oxonium ion opens the ring and generates a new oxonium ion,



The propagation reaction is very similar:



In these reactions Burrows (*87*) pictured the positive charge carried by each polymer chain as being balanced by an anion derived from the catalyst which was believed to be directly associated with the growing end of the polymer

chain. The system does not have a great deal of energy available as a driving force, so the ion pair was pictured as the means of minimizing the energy requirements for the reaction. This makes the nature of the anions quite important, because as nucleophiles they compete with the monomer in the propagation step.

The polymerization reaction is pictured to reach a mobile equilibrium occurring between the THF monomer and the oxonium-ion-terminated polymer. So the product would be a "living" polymer because of the ability to remain indefinitely active. Actually, though, termination occurs through reactions with impurities, with the counterion, or with quenching agents.

Dreyfuss and Dreyfuss (*89*) reported that tetrahydrofuran can be polymerized in bulk with *p*-chlorophenyldiazonium hexafluorophosphate catalyst. The resultant polymer was observed to be a "living" polymer (as above).

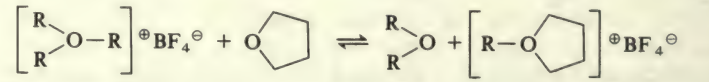
In a subsequent study on the reaction of 2-methyltetrahydrofuran with *p*-chlorophenyldiazonium hexafluorophosphate (*90*) it was found that the product contained 1 mole of nitrogen and 1 mole of chlorobenzene per mole of the salt. This suggested that the primary initiation reaction involved hydrogen abstraction by a chlorophenyl cation. So added to the polymerization mixture were compounds possessing labile tertiary hydrogens to determine whether this would enhance catalytic activity. However, it was found that the resultant polymers had virtually the same intrinsic viscosities as the products of polymerizations without these compounds. But, if there was a tertiary hydrogen alpha to an ether oxygen, a marked effect was observed. Also, when diethyl ether was used, which possesses no alpha hydrogen, a catalytic effect was observed.

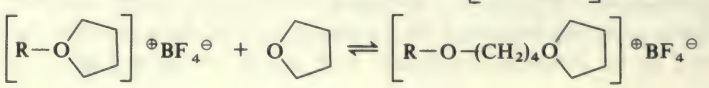
The catalysts for tetrahydrofuran polymerization can be separated into four categories (*87*).

Oxonium Ions

These are combinations of Lewis acids and strained cyclic ethers originally employed by Meerwein et al. (*84*). Boron trifluoride can be reacted in situ with epichlorohydrin to form the catalyst. Later, other Lewis acids and strained ring compounds were shown to be effective catalysts as well. Saegusa and co-workers (*91*) termed the cyclic ethers "promoters" for these polymerizations.

The oxonium salts may be convenient sources of the carbonium ions which transfer from the oxonium ion to the tetrahydrofuran monomer in a preliminary first step. Vofsi and Tobolsky (*93*), who determined the absolute rate constants for initiation and propagation, picture the reactions to be

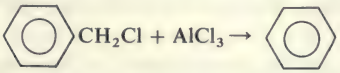
1. 

2. 

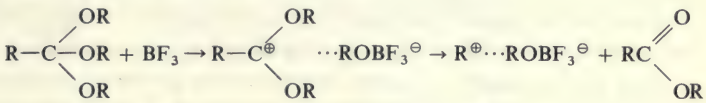
Carbonium Ion Generators

A number of systems appear to be a convenient source of carbonium ions by transferring labile nucleophilic groups from organic compounds (cocatalysts) to strong acids (catalysts) (*81*). Such systems, for example, are

$$CH_3{-}O{-}CH_2Cl + FeCl_3 \rightarrow CH_3{-}O{-}CH_2^{\oplus}FeCl_4^{\ominus}$$



$$R{-}OSO_3R + BF_3 \rightarrow R^{\oplus} + ROSO_3BF_3^{\ominus}$$



$$HClO_4 + CH_3{-}\overset{\overset{O}{\|}}{C}{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH_3 \rightarrow CH_3{-}\overset{\overset{O}{\|}}{C}^{\oplus}ClO_4^{\ominus} + CH_3\overset{\overset{O}{\|}}{C}{-}OH$$

Here there is competition between the Lewis acids and the carbonium ions for the nucleophile that is transferred. The polymers obtained are usually low in molecular weight. Brawn et al. (*92*) obtained high-molecular-weight products, however, by employing a previously isolated tropilium salt of antimony hexachloride as well as a triphenylmethyl carbonium antimony hexachloride as initiators:

Protonic Acids

Meerwein et al. have shown that potentially any strong electrophile is a catalyst if its counterion is a very poor nucleophile (*84*). Thus they were able to use strong acids, such as the fluorosulfonic and tetrafluoroboric acids already mentioned, which function by means of the secondary oxonium ion.

Lewis Acids

Most strong Lewis acids, such as $SbCl_5$, PF_5, and BF_3, will convert tetrahydrofuran to solid polymers without the aid of cocatalysts.

5-10. Electrically Controlled Anionic Polymerizations

Work by Breitenbach and Srna (*94*) and Funt and co-workers (*95–97*) demonstrated that passage of electric current through solutions of monomers in suitable solvents produced species that initiated polymerizations. Most of these were polymerizations by free-radical mechanism (*94*, *95*, *98*).

Yamazaki and co-workers (*99*) carried the reactions out in tetrahydrofuran using $LiAlH_4$ or $NaAl(C_2H_5)_4$ as the electrolyte and formed a "living" polymer from α-methyl styrene. The deep-red color of the anion first developed at the cathode compartment of a divided cell. The solution was then cooled to −80°C, resulting in an almost quantitative yield of a high-molecular-weight polymer ($\sim 10^4$). From their results, they concluded (*99*) that the mechanism of polymerization was identical to "living" polymerizations described by Szwarc et al. (*54*).

Funt and co-workers (*100*) were also able to polymerize styrene under similar conditions. Addition of naphthalene to the solution in the absence of monomer produced the typical green color of naphthalene complex. Subsequent addition of styrene produced the orange polystyryl anions immediately.

In a similar study of methyl methacrylate polymerization (*101*), it was found that polymerization could be best carried out in dimethylacetamide containing quaternary ammonium salts. Polymer formation was directly dependent on monomer concentration and square root of impressed current. Molecular weights of 50,000 were obtained.

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6

Polymerization with the Aid of Complex Catalysts

The complex catalysts used for addition polymerizations of olefins are:

1. The catalysts, commonly known as *Ziegler–Natta catalysts*, which are products from reactions of (a) metal hydrides or (b) metal alkyl reducing agents or alkylating agents with reducible metal halides. These catalysts can be soluble in the reaction medium (homogeneous) or insoluble (heterogeneous).
2. Insoluble coordinated complex catalysts which are reduced transition-metal oxides on some solid support such as carbon black, or silica or alumina or on a mixed bed such as silica–alumina.
3. "Alfin" catalysts, commonly used for diene polymerization.

The particularly important aspect of the complex catalysts is the fact that they often offer steric control in olefin polymerizations, making it possible to form linear polyethylene at low pressures, as well as isotactic polypropylene, and so on.

6-1. Ziegler–Natta Catalysts

The early experiments in this field can be credited to Ellis (*1*), who polymerized olefins with the aid of lithium alkyls in the presence of a hydrogen contact catalyst, such as nickel or nickel oxide on silica.

In 1954 Ziegler and co-workers (*2*) were able to form low-molecular-weight polymers from ethylene by using triethylaluminum as the catalyst. Their products ranged in molecular weights from 1000 to 5000. Then, after a series of experiments with similar materials, Ziegler evolved a system for polymerization of ethylene (*3*). This consisted of adding titanium tetrachloride to a solution of diethylaluminum chloride in xylene or in Fischer-Tropsch diesel oil, first forming a brown precipitate. Ethylene was then bubbled into this suspension for perhaps 30 minutes, sometimes at room pressure or at a few atmospheres.

The method yielded an all-linear or an almost-all-linear polyethylene of high molecular weight, sometimes as high as 3,000,000. This development was the start of much work on the coordination (complex) ionic catalysts.

Since then it has been found, after many investigations by numerous research workers, that the best catalysts are metal salts of Groups IV, V, and VI in the periodic table, including thorium and uranium. Of these, the most effective appear to be vanadium, zirconium, and titanium. Metals of Group II, copper, silver, and gold, appear to have no effect. These catalyst salts, usually halides, are used with organometallic compounds of Groups II and III metals. Most useful of these are Al, Zn, and Mg as alkyls, or alkyl halides, or alkali metal alkyls and alkali metal hydrides. Extreme examples of such could be $Li[Al(CH_3)_2H_2]$ and $Mg[Al(C_2H_5)_2H_2]_2$. But, in spite of this large group of such potentially useful catalysts, the more commonly used systems consist of trialkylaluminum with titanium tetrachloride or titanium trichloride.

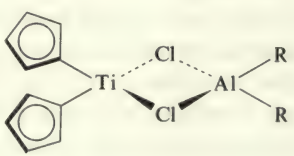
The reaction occurring between aluminum alkyls and titanium halides was investigated by various chemists. It is generally agreed that it proceeds according to the scheme (*4–6*)

$$TiCl_4 + AlR_3 \rightarrow TiCl_3R + AlR_2Cl$$
$$TiCl_4 + ClAlR_2 \rightarrow Cl_2AlR + TiCl_3 + R\cdot$$
$$TiCl_4 + 2AlR_3 \rightarrow TiCl_2R_2 + 2AlR_2Cl$$
$$TiCl_2R_2 \rightarrow TiCl_2R + R\cdot$$
$$TiCl_3 + AlR_3 \rightarrow TiCl_2R + AlR_2Cl$$
$$TiCl_2R \rightarrow TiCl_2 + R\cdot$$
$$TiCl_2R + AlR_3 \rightarrow TiClR_2 + AlClR_2$$
$$TiCl_2 + AlR_3 \rightarrow TiClR + AlClR_2$$

It might be added that only a few products of the above reactions have by now been isolated in pure crystalline form. One of them is bis(cyclopentadienyl) titanium dichloride–triethylaluminum: $(C_5H_5)_2TiCl_2Al(C_2H_5)_3$. This blue crystalline compound will form on combining dicyclopentadienyl titanium dichloride with triethylaluminum in heptane.

Two other similar compounds are known—$(C_5H_5)_2TiCl_2AlCl(C_2H_5)_2$ and $(C_5H_5)_2TiCl_2AlCl_2$. These soluble blue complexes are reported to be very active catalysts for ethylene polymerization when freshly prepared.

The structure of the bis(cyclopentadienyl) titanium dichloride aluminum dialkyls can be pictured as titanium possessing 3+ valence (*7,8*),



There is some indication in the literature, however, that maximum catalytic activity actually occurs when titanium is in the valence state 2+ (*9*). Thus, although the above-shown dicyclopentadienyl compounds contain titanium in the 3+ valence state, they are apparently only effective catalysts for ethylene (*10–13*). The coordination catalyst is, therefore, usually pictured as (*14–16*)

where R is an alkyl group, X is halogen, and M is Ti or V in 2+ valence form.

The aluminum and the transition metal are apparently joined by electron-deficient bonds. This appears to be at least true in the case of the bis(cyclopendadienyl) titanium dichloride studied by Natta et al. (*10*). Many of these catalysts have to be used immediately upon preparation and often have a finite time of decay of activity.

Some authors prefer to separate these catalysts into two categories: (1) the so-called *Ziegler catalysts*, meaning the reaction products of $TiCl_4$ with AlR_3 or $Al(R_aX_b)$ (where X is a halogen); these products exhibit less stable catalytic activity with time than the other category; and (2) the so-called *Natta catalysts*, which are prepared from $TiCl_3$ with AlR_3 or AlR_aX_b. The second catalytic system was shown to improve with time (*11*), reaching a maximum in about 2 hours. Furthermore, the $TiCl_3$-based catalysts were reported to yield more crystalline polypropylene, the amorphous portion occurring as stereoblocks in the polymer chains (*17*).

Various investigators also reported the effect of adding different compounds to these catalytic systems. Thus catalytic activity was shown to be enhanced toward α-olefin polymerizations by the addition of small amounts of oxygen, aromatic compounds, or electron donors such as amines, with the products possessing a greater amount of stereoregularity (*18–20*).

Overberger and Jarovitzky (*21,22*) feel that there might exist one significant difference between the Ziegler and Natta catalysts, in that although both produce insoluble titanium alkyls during the process of their formation (these being tri- and perhaps bivalent), the Ziegler system also produces soluble tetravalent titanium alkyls that can adsorb and/or chemisorb onto the in situ–formed tri-(di-)valent titanium alkyl surface. These adsorbed and/or chemisorbed materials, they believe, might also have catalytic activity towards polymerization of α-olefins, but perhaps not to the same high steric order that is obtainable from active centers derived from the surface proper.

Generally, most such heterogeneous systems are active at relatively high temperatures (room to 100°C) when an aluminum-to-titanium ratio of 2 or 3 to 1 is used.

When a $TiCl_4$—$Al(C_2H_5)_3$ system based on an aluminum to titanium ratio of 1:1 is used, however, at the same or even higher temperatures, only low molecular weights and/or amorphous polymers result. But these same catalytic systems, when used at −78°C, will yield stereoregular polyvinyl ethers (*23*) and stereospecific poly(α-methyl-styrene) (*24*). $TiCl_4Al(i\text{—}C_4H_9)_3$ was reported to yield polyethylene (*25*) at −78°C and polypropylene at −30°C.

Overberger and Jarovitsky suggest (*22*) that $TiCl_4$ (and perhaps $TiCl_3$) initially forms, in conjunction with $Al(R_aX_b)$, ionic species from Lewis acid-base reactions which subsequently with time and/or applied temperature are transformed into soluble- and/or insoluble-alkylated titanium moieties. They caution, however, that positively charged titanium species, when occurring as part of a surface in the form of active centers (that is, alkylated or not alkylated, respectively) must form a relatively tight ion pair with an $Al(R_aX_b)$ anion. This is supported by the fact that polymerization of vinyl cyclopropane with $TiCl_3$—$Al(i\text{—}C_4H_9)_3$ resulted in unrearranged and crystalline poly(vinyl cyclopropane) (*26*).

6-2. Mechanism of Polymerization

The mechanism of the Ziegler–Natta catalyzed polymerization is still subject to debate, and our understanding of it is evolving now. So, as is common to such situations, a number of different versions were proposed to explain the mechanistic path. Many investigators agree, though, that polymer growth takes place at the metal-carbon bond of the metal alkyl. Disagreement still exists about the mechanism: Is it monometallic or bimetallic; what is the exact placement of the metal alkyl in the complex; and by what means is the olefin placed (*22,27–37*)?

Natta proposed (*29,30*) that the active catalyst is a complex between a transition metal halide with valency less than the maximum and a metal alkyl of Groups I to III. The metal alkyl bond is highly polarized in the direction of the carbanion and the monomer units are inserted between such a metal-carbanion bond, thus giving rise to anionic polymerization in which the growing anion is coordinated with the metal cation,

$$M^{\oplus}\overset{\ominus}{C}H_2R + CH_2{=}CH_2 \rightarrow \overset{\oplus}{M}\begin{matrix}\vdots\\ \overset{\ominus}{C}H_2{-}\overset{\oplus}{C}H_2\end{matrix} \quad \overset{\ominus}{C}H_2R \rightarrow M{-}CH_2CH_2CH_2R \rightleftharpoons \overset{\oplus}{M}\overset{\ominus}{C}H_2CH_2CH_2R + \text{etc.}$$

Natta has shown that the precipitated insolubles $TiCl_3$ and $TiCl_2$ will complex or absorb a certain amount of excess AlR_3. Such a catalyst can be reactivated by continuous addition of the triethylaluminum.

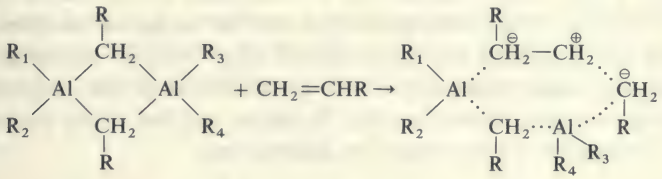
Eirich and Mark (*28*) offered equations which related the polymerization rate to the strength of monomer absorption, to the nature of the complexed catalyst, and so on. Several systems conformed to this relationship. On the other hand, many contradictory systems were also found.

The possibility of free-radical mechanism was speculated on, but Natta presented strong evidence against it. He demonstrated that (1) it is possible to form block copolymers with alternate feeding of different monomers, even when polymerization is interrupted; and (2) the polar effects of substituents in the series of vinyl aromatic monomers is actually opposite to that known in radical polymerization.

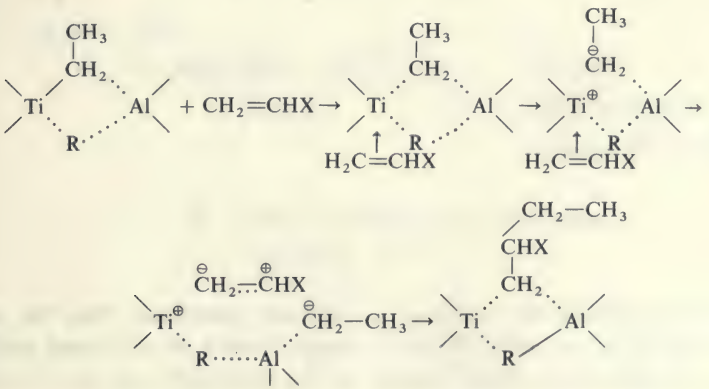
Thus Natta pictured the mechanism of polymerization in terms of electron-deficient complexes (*38*) as follows.

Initiation: The metal alkyl and the monomer are both adsorbed on the catalyst surface and compete for available sites with the active centers formed from reduced titanium halide and aluminum alkyl. The initiation takes place between the adsorbed alkyl and the neighboring adsorbed or unadsorbed monomer. The number of active sites would depend upon the amount of reduced metal halide present in the system.

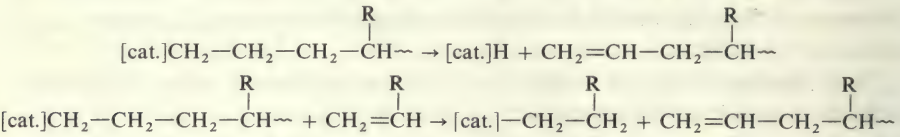
Propagation: Natta originally postulated (*39,40*) that the adsorbed monomer is inserted between the metal and the alkyl portions of the aluminum alkyl. This type of "insertion" hypothesis required that two bonds be broken and two bonds be formed simultaneously in each step,



In more recent papers (*38*), however, Natta and co-workers concluded that the active sites are actually made up of titanium or vanadium which form bridged complexes with aluminum alkyls. In the initiating step the titanium atoms coordinate with the olefin. The driving force for the propagation is the coordination of the olefinic electrons with the vacant hybrid *d*-orbitals of the titanium, the olefin adding to the aluminum-carbon bond,



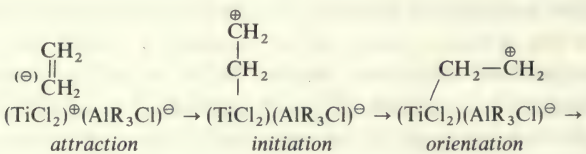
Termination: Termination is believed by Natta and Pasquon (*38*) to occur by spontaneous disproportionation or by transfer to a monomer. In both cases a hydride ion would be involved:

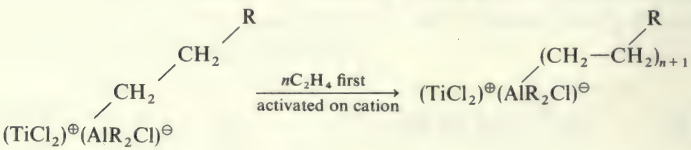


Uelzmann proposed a somewhat different mechanism (*32*), based on an ion-pair structure. He starts with the $(TiCl_2)^{\oplus}(AlR_3Cl)^{\ominus}$ complex and suggests that the monomer is activated on the Ti cation, the positive end orienting to the negative complex ion. This, theoretically, allows the carbonium ion to neutralize its charge in two ways:

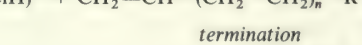
1. The $R^{\ominus}$ migrates out of the complex and adds to the ion to form $Cl_2Ti-CH_2-CH_2^{\oplus}$.

2. Because the complex-stabilized $R^{\ominus}$ has no tendency to leave its stable state to form a less stable compound, it neutralizes the activated system by pulling the ethylene by its carbonium ion into the negative complex. By this migration of the activated monomer the $(TiCl_2)^{\oplus}$ ion is reformed and the growing polymer chain stabilized in the complex ion at the same time. The next monomer is again initiated on the Ti cation and the whole process starts once more. Termination is by hydrogen abstraction:





migration and propagation



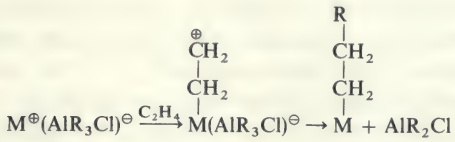
termination

From the mechanism he presented, Uelzmann postulates that the polymerization would be prevented when Ti could form a M—C bond with an alkyl group of aluminum alkyl, because of the destruction of the Ti cation

according to the reaction

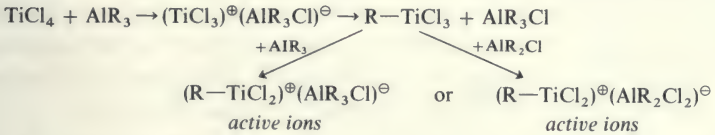
$$M^{\oplus}(AlR_3Cl)^{\ominus} \longrightarrow M{-}R + AlR_2Cl$$

or



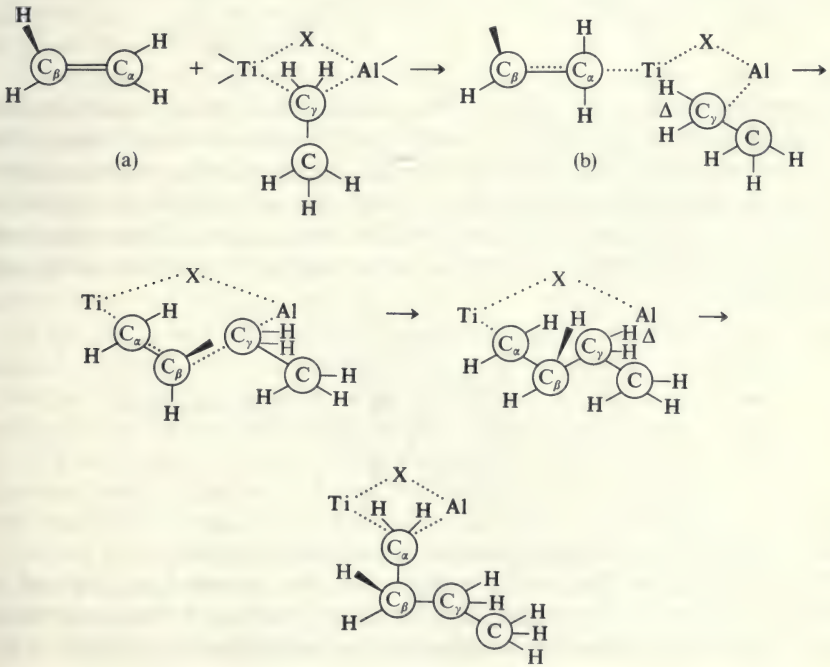
where M is a transition metal.

But when the titanium alkyl is stable enough (at low temperatures) to react again with aluminum alkyl, it can form another pair of active ions,



Independently, Bier (*41*) proposed a somewhat similar mechanism, also based on ion pairs.

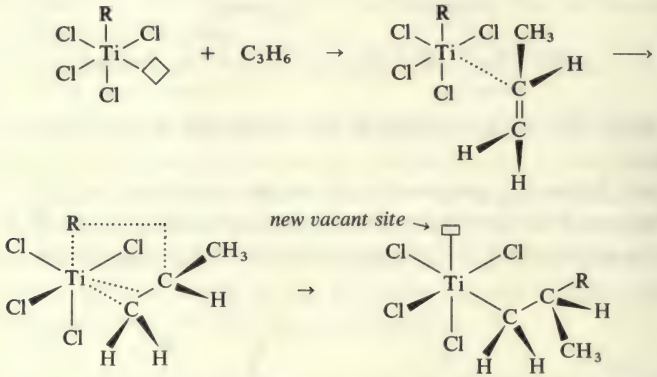
Patat and Sinn (*42*) proposed a working hypothesis of the low-pressure polymerization of ethylene with the Ziegler-type catalysts which was based on the idea of a single bond rupture for monomer occurring during insertion,



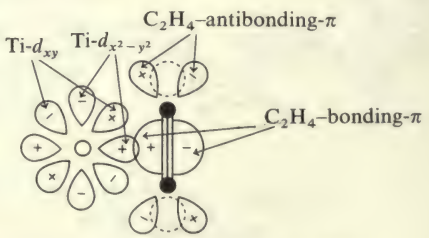
In a later paper (*43*) dedicated to the mechanism of the action of organometallic catalysts, Sinn and Patat drew a similar mechanistic picture for catalysts based on bis(cyclopentadienyl) titanium compounds.

Here they assumed that the complex formed from the organotitanium and organolithium compounds contains a halogen bridge and a carbon bridge and that it is an electron-deficient compound.

Cassee (*44*) disagreed with other proposed mechanisms and felt instead that the polymerization occurs at one titanium ion on the surface layer of a titanium trichloride (or presumably dichloride) crystal lattice. One surface chlorine atom is replaced by an alkyl group R and an adjacent chlorine site is vacant to accommodate an incoming monomer molecule. Polymerization would then proceed in a fashion similar to one originally suggested by Ludlum and coworkers (*45*),



Upon completion of this step a titanium alkyl bond and a vacant site are retained by the active center. The vacant site, however, changes places in the course of the reaction. The alkyl aluminum is relegated to the role of a chain-transferring agent, reestablishing lost centers and acting as a scavenger for impurities. It is not believed to be essential for propagation. Cassee represents the driving force for the polymerization as a π-type olefin complex, which can be pictured



which is a diagrammatic representation of an orbital overlap.

The π-electrons of the olefin overlap with the vacant $d_{x^2-y^2}$ orbital of titanium, resulting in formation of a transitory π-bond. At the same time, the d_{xy} orbital of the metal can overlap the vacant antibonding orbitals in the

olefin and thereby cause a decrease in the distance between the highest filled bonding orbital and the empty (or nearly empty) *d*-orbital of t_{2g}-type. Such a situation was demonstrated by Chatt and Shaw (*46*) to lead to a weakening of the carbon-metal bond and consequently cause migration of the alkyl group to one end of the incoming olefin molecule in alkyls of transition metals.

Bawn and Ledwith (*47*), in reviewing the various proposed mechanisms, concluded that essentially all ion-pair mechanisms can be typified by the Uelzmann suggestions (*32*). Such a mechanism could serve as a basis for most other mechanisms because:

1. The actual chain growth takes place by coordination of the monomer with the transition metal and thus accommodates the findings of Carrick et al. (*15*), who showed that the relative reactivity ratio of two monomers, ethylene and propylene, in copolymerization changed when different transition-metal compounds were used, but was not affected by the use of different reducing agents when used with the same transition metal.

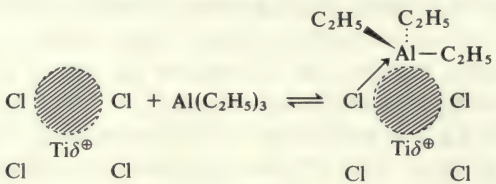
2. The aluminum alkyl is essentially a chain carrier and this could account for the conclusion of Natta et al. (*48*) that the chain grows from the aluminum-carbon bonds, and, in addition, could dispose with the objection that titanium-alkyl bonds are not sufficiently stable to exist through the lifetime of a growing polymer chain.

3. A mechanism based entirely on a crystal lattice, such as Cassee's (*44*), would require only slight modifications to incorporate an ion-pair propagation, because the fundamental reaction between monomer and reduced titanium halide cation would be essentially the same as that proposed for the neutral alkylated titanium halide molecule.

4. Ion-pair mechanisms of this type adequately explain the enormous catalytic influence of small amounts of titanium halides on the "aufbau" reaction of aluminum alkyls. The latter point has been suggested by Ziegler (*49*).

An interesting series of papers on coordination catalysis were published by Boor (*50*), who felt at first that results of his work (*51*) pointed strongly to a bimetallic mechanism. He studied the dependence of the Ziegler polymerizations of olefins on the structures of the metal alkyls and on the transition-metal compounds. The catalysts he used were based on $(C_2H_5)_2Zn$, $(C_2H_5)ZnCl$, and $Cd(C_2H_5)_2$, in combinations with one linear and several layer-type titanium chloride crystals. The polymerizations were conducted on propylene and 1-butene. All but one α-$TiCl_3$ of the titanium chlorides contained $AlCl_3$ in solid solution. Changes in the activity and steric control of the various catalysts as well as changes in the molecular weights of the formed polymers were observed with variations of several parameters. These parameter variations were changes in concentrations of the metal alkyls and the titanium chloride, variations in reaction time and temperature and variations in pressure of the olefins. The fact that these led to changes in products led Boor to feel (*50*) that this supports the view that the structure of the metal alkyl or the transition-metal compound is predominately important in determining the ability to

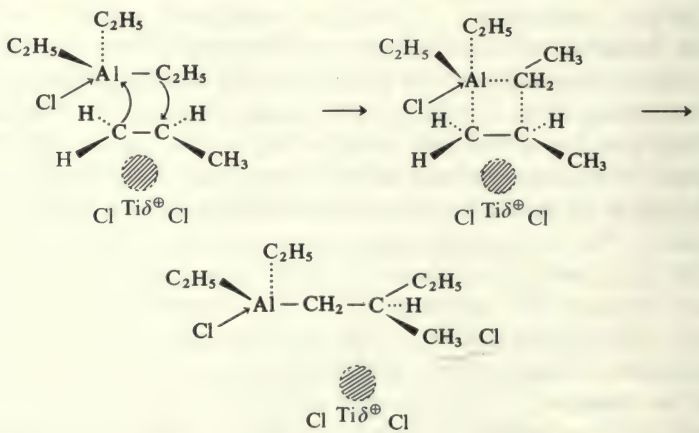
exert steric control, to the extent that there must be an interaction between components in the presence of the olefin to modify the crystal surface. He suggested that the active sites on the catalyst crystal are regions of exposed transition-metal atoms which possess differing capacities for complexing with electron donors, such as the olefin. Earlier studies (*52*) suggested strongly that the detailed structure of the transition-metal compounds played an intimate role in the stereospecific process. Specificity of the catalyst was attributed by Boor to the different geometrics of the exposed titanium. So he concluded that only exposed titanium along the edges of the crystal can favor stereospecific growth. Thus he preferred reactive sites consisting of exposed transition-metal atoms coordinated with the metal alkyl molecules through halogen bridges,



chlorine vacancy and a pentacoordinated titanium

bimetallic reaction complex

The exposed transition metal then functions to complex the olefin in the primary step. The electron density at the double bond is lowered as result of this and the double bond also becomes polarized. The concerted process by which the metal alkyl then reacts with the olefin, such as a polypropylene, requires only small nuclear displacement,



Only those complexed propylenes that are in juxtaposition to assume this transition state will be interposed into the Al—C bond. This position of the complexed metal alkyls was believed by Boor to be of utmost importance in deciding which of the complexed olefins will be consumed. If large nuclear displacements are required, then that particular complexed propylene will

not be in a favorable position for the concerted process to occur. The unsubstituted carbon of the olefin couples with the aluminum as suggested by others, but the driving force for the olefin-complex formation is the attainment of a titanium coordination number of 6.

So the propagation then proceeds, as originally pictured by Boor, in two stages: formation of the bimetallic reaction complex, and passage through the transition state as pictured above. Termination occurs by displacement and disproportionation as originally pictured by Natta and Pasquon (*38*) and by Ziegler (*2*).

Evidence that became available within the last several years, however, caused Boor to change his mind in favor of the monometallic mechanism (*53*). He sought direct experimental evidence (*54*) by adding certain alkyl chlorides (*t*-butyl chloride, *s*-butyl chloride, allyl chloride, methallyl chloride, and benzyl chloride) to both, a conventional Ziegler catalyst and to two metal alkyl-free catalysts. The effects on catalyst activity and specificity as well as on the molecular weight of the formed polymer were then compared.

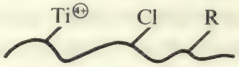
The significance of the comparison lies in the fact that a metal alkyl–free catalyst functions ostensibly as a monometallic initiator. Should the conventional Ziegler catalyst also function through a monometallic mechanism, then there should be similar effects from the added alkyl chlorides. And Boor expects that if the Ziegler catalyst functions by a bimetallic mechanism, then differences in effects from additions of the alkyl chlorides should manifest themselves. This is based on his reasoning that the effects would be similar if the sites are monometallic in both types of catalysts, because the Ti—C bond sites, being buried in the chlorine vacancy, will not be very accessible to the RCl molecule and therefore will be expected to show preferential reactions toward differently structured RCl molecules. The order in which a series of alkyl chlorides will affect the catalysts should then be characteristic of the monometallic site. This order, he felt should be different from the order in which the same series of alkyl chlorides would affect the catalyst, should the sites be bimetallic, because in a bimetallic complex site the M—C bond-growth site contains a different metal and is highly exposed to RCl reaction.

Boor's results indicated that the effects of various organic chlorides on polymer conversion, molecular weight, and isotacticity were indeed similar for both a Ziegler-catalyst system and for two metal alkyl–free catalysts. These results led Boor to conclude that the evidence strongly suggests that the sites in both types of catalysts have similar structures, and that the metal alkyl in a Ziegler catalyst does not become an integral part of the active site, and also that metal alkyl molecules that are chemisorbed on the crystal surface may, perhaps, influence catalyst behavior indirectly; for example they may hinder (or promote) cleavage of the crystal, and in this way may affect the polymerization rate.

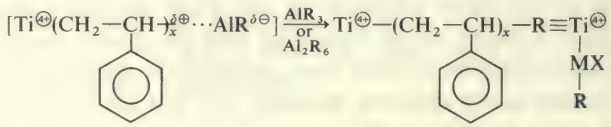
A different explanation of the reaction mechanism of coordination catalysis was offered by Overberger and Jarovitzky, who studied the polymerization

of styrene (*22*). They observed that the reaction of $TiCl_4$ and AlR_3 (or AlR_aX_b), which takes place in the absence of monomers, results in at least two distinct types of products: (1) formation of tri- and/or bivalent alkylated-titanium surfaces,

and (2) formation of soluble, tetravalent alkylated-titanium species ($Ti^{\oplus\oplus\oplus\oplus}—R_n$). The latter can be adsorbed and/or chemisorbed onto the surface,



Overberger and Jarovitzky feel that in such a catalyst system the initial process of the choice of potentially active centers depends on the nature of the monomers employed. Monomers, such as styrene, which can form relatively stable carbonium ions, or those which are susceptible to cationic polymerization, will initiate chain growth by using potentially active centers of highest ionic character such as solutions of $Ti^{\oplus\oplus\oplus\oplus}$, $TiCl_3\delta^{\oplus}$, $TiCl_2\delta^{\oplus}R$, and so on. The process of initiation would then be another means of forming active centers through alkylation of the titanium by the monomer. They suggest that these reactions produce species of the general structure



where k may be unity or larger, depending upon the ease with which the monomer undergoes cationic polymerization and/or on the speed with which an ($R^{\ominus}$) group can be transferred from the aluminum alkyl counterion or from an excess AlR_3. Then these monomer-alkylated titanium species found in solution with the Ziegler catalysts end up by being adsorbed and/or chemisorbed to the surface of $Ti^{\oplus\oplus\oplus}—R$, or they undergo bimolecular disproportionation in solution among themselves and even during sorption with a species of already adsorbed and/or chemisorbed $Ti^{\oplus\oplus\oplus\oplus}—R_n$ or $Ti^{\oplus\oplus\oplus\oplus}—(CH_2—CH)_x—R$.

It is also reasonable (*22*) that a decomposition of $Ti^{\oplus\oplus\oplus\oplus}—Mx—R$ species cannot result in a high-molecular-weight polymer. Instead the high-molecular-weight polymer comes from the propagation of $Ti^{\oplus\oplus\oplus\oplus}—Mx—R$ species on the $Ti^{\oplus\oplus\oplus}—R$ surface by a "coordinate-anionic" mechanism. In contrast to the cationic mechanism for the formation of active centers, a coordinate anionic mechanism should result in the insertion of a monomer between titanium and an alkyl group (—Mx—R). The latter mechanism, in sharp contrast to cationic initiation, should offer maximum steric control over the growing chain.

The approach taken by Overberger and Jarovitzky may explain some of the differences in homogeneous and heterogeneous catalysts.

6-3. Reduced Metal Oxides on Support Catalysts

Use of reduced transition-metal oxides such as MoO_3 on alumina, NiO_3 on charcoal, or V_2O_5 or CrO_3 on silica, as catalysts for olefin polymerization, evolved simultaneously with the Ziegler catalysis. These catalysts yielded high polymers of ethylene when used in suspension in various solvents, the reactions being carried out from 100 to 260°C under 50–15,000 pounds pressure. Mixed beds such as silica-alumina were also used. A typical catalyst preparation (*55*) would start with nickel nitrate solution in which nitric-acid-leached charcoal is first soaked. The charcoal, with the absorbed nickel salt, is then heated at high enough temperatures to decompose the nitrate, followed by reduction with either hydrogen gas or an alkali borohydrate. Sometimes powdered aluminum oxide or molybdena–alumina would be added before reduction. When silica–alumina support is used, the catalyst bed (16–30 mesh) is first treated with a 3% solution of the nickel nitrate, dried, and then heated to 500°C to decompose the nitrate. This again is followed by a reduction.

Although general use of Group VIA metals appears potentially possible, most of the work was done with the elements, Mo, Cr, V, Ni, and Co.

6-4. Mechanism of Polymerization

The mechanism of this type of polymerization is still not clear. There are indications that the mechanism may be different from that of Ziegler–Natta catalysis (*56–59*). Uelzmann originally proposed (*32*), however, that the two mechanisms are related. He pointed to the necessity of working with carriers such as alumina, which he felt indicated that this material plays an important part in the catalysis. This suggested to him that alumina probably forms the negative complex ion in which a propagation starter, such as $H^{\ominus}$, is introduced by a promoting agent (H_2 hydrides). Hydride formation on the carrier metal would yield metal alkyl by monomer addition. The transition metal then supplies the active cation for the initiation, which can be present in different valence states.

Guyot and co-workers (*60*) studied the influence of oxygenated impurities probably present in propylene on the polymerization kinetics of the CrO_3 on a silica-alumina support catalyst. As a result of this work they concluded that only a fraction of chromium atoms are active centers that could be in pentavalent form.

6-5. Alkyl-Promoted Transition-Metal Catalysts

One variation in the use of the transition-metal oxides as catalysts is to add aluminum alkyls as promoters. Now the catalyst system becomes $CrO_3 \cdot SiO_2$ promoted by R_3Al, or $V_2O_5 \cdot SiO_2$ promoted by R_3Al, etc. At present no general agreement exists as to the mechanism of such polymerizations (*61*).

Smith and Zelmer (*62*) studied the kinetic behavior of five transition-metal catalysts for ethylene polymerization: $CrO_3 \cdot SiO_2$ and $V_2O_5 \cdot SiO_2$ promoted by $(i\text{-}C_4H_{10})_3Al$; $VOCl_3$ promoted by $(C_2H_5)_2AlCl$; $TiCl_4$ promoted by $(C_2H_5)_3Al$ or $(i\text{-}C_4H_{10})_3Al$; and $(C_5H_5)_2TiCl_2$ promoted by $(CH_3)_2AlCl$.

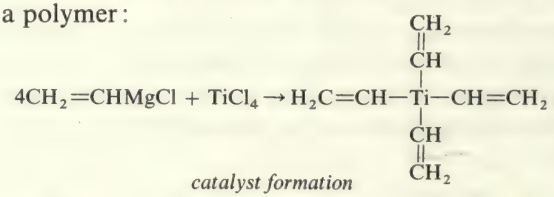
Despite obvious differences in the chemical nature of their active species, all these systems showed second-order deactivation of the active species with time. This suggested to them a unified concept for a mechanistic picture based on (1) complex formation between the transition-metal complex and the alkyl, (2) alkylation of the complex, (3) polymerization by the alkylated species, and (4) second-order decay of active species.

6-6. Organotransition Metal Catalysts

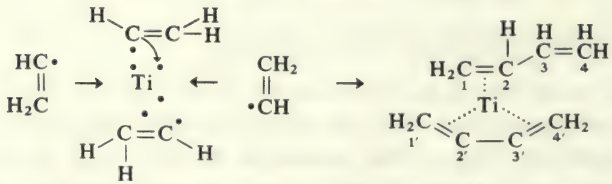
Tsutsui and Ariyoshi developed a catalyst system for polymerization of 1,3-butadiene based on stochiometric mixtures of a Grignard reagent and a transition-metal halide in a tetrahydrofuran system (*63*). The investigators originally considered this system to react by forming σ-bonded organotransition metals (*64,65*). Such compounds are believed to be true catalysts in the butadiene polymerization, with the MgX_2 formed during the reaction not participating in the catalysis as such.

Various degrees of conversion and steric controls were obtained by using a stochiometric mixture of methyl-, ethyl-, vinyl-, and phenylmagnesium halides with titanium tetrachloride.

Tsutsui and Ariyoshi now speculate (*63*) that the mechanism might proceed as follows: Tetravinyl titanium is formed at the first stage of the catalyst reaction. The σ-bonded tetravinyl titanium then rearranges to give a π-bonding complex. Internal dimerization takes place within the complex to give a π-bonded 1,3-butadiene-titanium complex. Dimerization takes place through coupling of carbons 2 and 4′, leaving radicals on carbons 1 and 3′. Another 1,3-butadiene molecule may then be attracted and form a π-complex with the titanium atom, and the radical on carbon 3′ of the dimer will attack the α-carbon atom on the 1,3-butadiene molecule. Thus a trimer is formed. Continued repetition of this process yields a polymer:



catalyst formation



rearrangement of tetravinyl titanium to give a π-complex

π-bonded 1,3-butadiene titanium complex

Catalytic actions of organic chromium, iron, cobalt, and nickel compounds were also investigated. Low-molecular-weight polymers were obtained in all cases (*63–65*).

6-7. Polymerization of Polar Monomers

Generally, coordination catalysts, such as the Ziegler–Natta systems, are used for polymerization of nonpolar olefins. Polar monomers such as vinyl chloride, methyl methacrylate, acrylonitrile, and so on, are reduced in the presence of these complexes. Etlic and co-workers (*66*) demonstrated, however, that these catalysts can be used to carry out vinyl-chloride polymerizations in satisfactory yields when nucleophiles are added to complex the catalyst and to lower the reducing capacity of the system. Vinyl chloride was also polymerized with these catalyses by Giannini and Cessea (*67*). Razuvayev and co-workers (*68*) studied the catalytic activity of a binary heterogeneous catalyst consisting of the α-form of titanium trichloride or chromium trichloride in a mixture with alkoxy-derived diethyl aluminum bromide or triisobutyl aluminum in polymerization of vinyl chloride. The best results were obtained with the addition of such strong electron donors as triethylamine. Pyridine, ethyl ether, and others produced poorer results.

Gaylord and Mark described a process for the polymerization of vinyl chloride and methyl methacrylate monomers using a heterogeneous catalytic system based on a mixture of triisobutylaluminum and vanadium trichloride in tetrahydrofuran. A variation on this method was to use triethylaluminum, an ester, and a vanadium compound (*55*).

Gritsenko and co-workers (*69*) reported polymerization of acrylonitrile over Ziegler catalysts by injecting polar compounds into the system to compete with the monomer, principally acetonitrile.

Sianesi and Caporiccio (*70*) also reported polymerization of perfluoro-olefins with the Ziegler–Natta catalysts.

6-8. Alfin Catalysts

The alfin catalyst is a heterogeneous or solid surface catalyst developed by Morton et al. (*71–75*). It is a reaction product of amyl chloride with sodium, which is then reacted with isopropyl alcohol. The result is a mixture of amyl sodium, sodium chloride, and sodium isopropoxide. Propylene is then bubbled into this mixture to convert the amyl sodium to allyl sodium:

$$C_5H_{11}Cl + 2Na \rightarrow C_5H_{11}Na + NaCl$$

$$\tfrac{1}{2}C_5H_{11}Na + \tfrac{1}{2}(CH_3)_2CHOH \rightarrow \tfrac{1}{2}(CH_3)_2CHONa + \tfrac{1}{2}C_5H_{12}$$

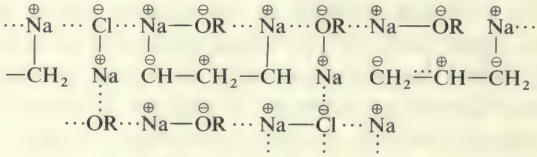
$$\tfrac{1}{2}C_5H_{11}Na + \tfrac{1}{2}CH_3{-}CH{=}CH_2 \rightarrow C_5H_{12} + CH_2{=}CH{-}CH_2Na$$

This catalyst was developed for use in butadiene, isoprene, and styrene polymerizations. The advantage of this catalyst system lies in the fact that

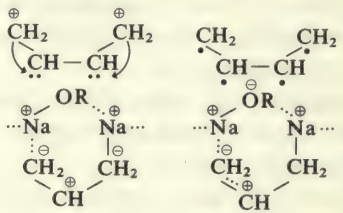
copolymerizations of butadiene and styrene can be carried out to yield 1:1 copolymers. This catalyst system also yields a very rapid reaction, with the products having very high molecular weights (1.5–2 million) of a fairly narrow distribution.

Polybutadiene prepared by alfin catalysis is 70–80% 1,4 adduct, similar to the products of free-radical polymerizations, with the double bond in the *trans* configuration. The polymerization is carried out at low temperatures (−15°C).

It was generally demonstrated that sodium chloride as well as all other components of the catalyst mixture are essential to the reaction. The catalyst bed can probably be pictured as follows:

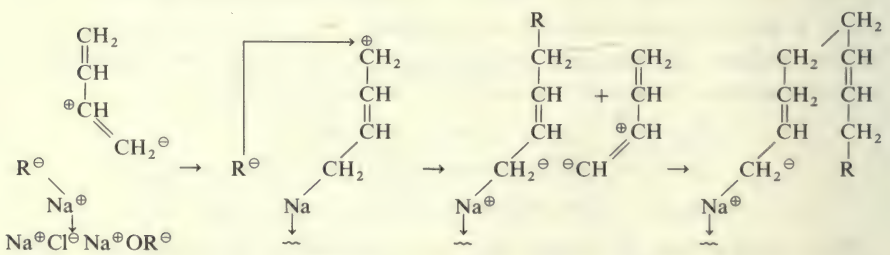


As seen from the above, there are extensive mesomeric possibilities, owing to resonance complexes or crystals formed with NaCl and NaO isopropyl. As a result, two centers are possible, a carbonium center and a radical center,



carbonium center *free-radical center*

An anionic mechanism, however, is generally pictured for this reaction,



catalyst bed *initiation* *propagation*

6-9. Copolymerization with Ziegler-Natta Catalysts

Copolymerizations carried out with Ziegler–Natta catalysts encounter the same problems as are found with other ionic catalysts. Nevertheless, copolymerization of nonpolar α-olefins is well known (*69*). These copolymers form at relatively low temperatures and pressures. Typical of these is the much-studied copolymerization of ethylene and propylene. Ethylene polymerizes much faster, so compensating measures must be employed to obtain homogeneous compositions. Actually, in spite of it, the products are still often quite heterogeneous in nature. Lukach and Spurlin (*76*) list the minimum requirements that must be met to obtain an ethylene–propylene copolymer of fairly uniform composition. These are a soluble catalyst system and control of monomer composition. Apparently different Ziegler–Natta catalysts can have widely different relative reactivities toward ethylene and propylene. The most satisfactory catalysts are based on soluble vanadium compounds of valence 3 or higher and alkylaluminum. One of the ingredients must contain halogen. It is preferable to add the ingredients separately to the reaction mixture in the presence of the monomer. The active catalyst has a short average lifetime, about 5–10 minutes, at 30°C.

Anderson et al. (*77*) studied copolymerization of styrene with α-olefins. By using α-$TiCl_3$-$Al(C_2H_5)_3$ as catalyst in toluene they produced copolymers of styrene with 4-methyl-pentene-1 and with 5-methyl-hexene-1. The copolymers were quite heterogeneous in composition. Statistical analysis showed that the copolymers were mixtures of block macramolecules, the chain backbones consisting mainly of one monomer type with short blocks of the other.

6-10. Copolymerization with Supported Metal Oxide Catalysts

Considerations which apply to copolymerization of olefins with the aid of Ziegler–Natta catalysts are similar to those which apply to copolymerizations with support metal oxides. Thus the rate of ethylene vs. propylene polymerization over chromium oxide on silica-alumina, activated at 540°C, is roughly 100:1. The same is true for the relative copolymerization rates of ethylene and 1-hexene. In spite of that, some α-olefins, such as 1-butene, will copolymerize at a higher rate than they will homopolymerize, allowing for a greater incorporation of the comonomer than would be expected.

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Stereospecific Polymerization 7

In previous chapters the mechanisms of addition polymerizations were discussed. No emphasis was directed, however, toward the means for attaining steric specificity in the products. As this is an important aspect of synthetic approaches, this subject will be brought up here. Stereospecific polymerizations received constantly increasing attention over the last 10 years and at least one very excellent review article (*1*) has appeared in the literature.

Mihail and Herscovici (*2*) postulated the essential requirements for polymerization conditions which lead to steric controls. These are:

1. To form stereoregular molecules there should be orientation at an interval between the reactive part of the monomer and the reactive center greater in length than is characteristic of the transition state.
2. The act of addition of the monomer to the propagating chain must in itself be essentially stereospecific; that is, it should be a reaction controlled by steric factors.
3. The terminal phase of separation of the molecule formed from the reaction center must occur under conditions so controlled that the addition of a new monomer molecule would take place in the same sequence.

These three requirements appear to be general for all three types of polymerizations: free radical, ionic, and coordination. However, each has its peculiarities in the manner in which some or all of these conditions may be met and should, therefore, be considered separately.

7-1. Steric Control in Free-Radical Polymerization

In free-radical polymerization the propagating radical chain is not restricted by the presence of a counterion nor is it usually influenced strongly by the solvent. This method of polymerization should offer, therefore, the greatest amount of freedom to the propagating species, so any control that the reaction conditions can exercise over the propagating species would increase at lower

temperature simply because of the low mobilities of the species. This was predicted by Huggins in 1944 (*3*) and demonstrated to be so by Fox and co-workers (*4*), who found that free-radical polymerizations conducted at very low temperatures yielded polymers with considerably greater degrees of stereoregularity than those conducted at elevated temperatures.

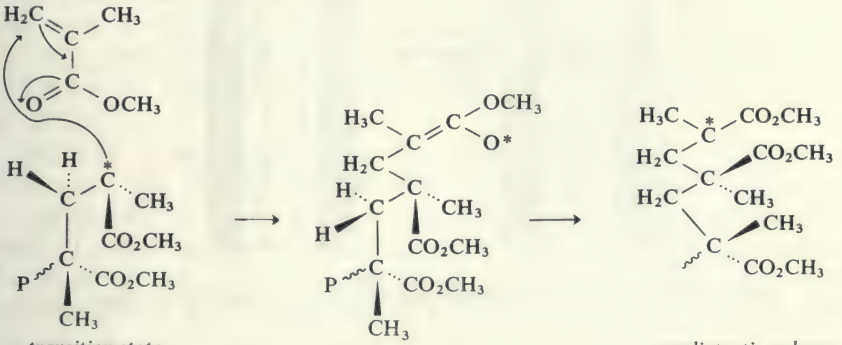
An interesting study was then conducted by Fordham (*5*), who correlated qualitatively stereoisomerism of vinyl polymers with rotational isomerism in simple compounds, as both are subject to placement and interactions of the substituent groups. This led him to conclude that in a representative free-radical polymerization, the activation energies of syndiotactic and isotactic propagations are very probably related to the relative potential energies of the respective configurations, because the activation energy of radical addition is lowered with increased heat of the exothermic reaction. He also calculated the potential-energy levels for the steric and electrostatic components of the two respective configurations. These calculations enabled him to show two syndiotactic (a) *trans-trans* and (b) *gauche-gauche* and one isotactic (c) *trans-gauche* structure of which the *trans-trans* has the lowest energy level. Because of the low energy of *trans-trans*, the preferred conformation would then be syndiotactic placement, which should be *trans-trans* with respect to carbon atoms in the chain, yielding the planar zigzag backbone. This was actually observed experimentally by Natta et al. (*6*) for 1,2-poly(1,3-butadiene) and by Fordham and co-workers for poly(vinyl chloride) (*7*).

A detailed study of the number and length of syndiotactic sequences in poly(methyl methacrylate) was carried out by Bovey (*8*), who used nuclear magnetic resonance techniques. He demonstrated that syndiotactic propagation becomes increasingly dominant with the decrease in polymerization temperature, and an increase in temperature is accompanied by an increase in randomness.

Fordham et al. (*9*) concluded from an investigation of free-radical polymerizations of a series of halogenated vinyl acetates that generally electrostatic factors during free-radical polymerization exert greater influence than steric factors on the resultant steric arrangement of the polymer, and, as only syndiotactic polymers are known from stereospecific free-radical polymerizations, they also concluded that syndiotactic propagation might be preferred for all free-radical polymerizations.

Cram points out that syndiotactic placement should predominate in free-radical polymerizations (*10,11*) from considerations of steric effects in reactions of small molecules. He assumes that the effective bulk of the substituents near the reactive center should fall in the order $\sim\!\!\sim P_n > CO_2CH_3 > CH_3$, where $\sim\!\!\sim P_n$ represents the polymer chain. Thus the least internal steric compression within the macromolecule will be reached when the growing radical end and the penultimate monomer unit adopt the configuration where * indicates a lone electron or a negative charge. This, as shown, leads to a syndiotactic structure which will be independent of the approach of the incoming monomer.

Burleigh et al. (*12,13*) observed an effect by the solvent on free-radical propagation when they found that syndiotactic poly(vinyl chloride) can be formed by carrying out the polymerization in an aliphatic aldehyde medium at 50°C.



transition state *syndiotactic polymer*

Solvent influence on all types of polymerization reactions in general were studied by Szwarc (*14*) and Ham (*15*). Both find helix formation for macromolecules when they are in the crystalline state as well as when they are dissolved in very "poor" solvents of low solvating power. This led Bawn and Ledwith (*1*) to propose that if a "poor" solvent is used during polymerization, then a growing polymer molecule might take up a helical form, such as might be obtained in the crystalline polymer. If a regular helix does form in the process of chain growth, then a particular steric configuration of asymmetric carbon atoms could result (owing to the desirability of preserving the symmetry of the helix), leading to steric control in the resultant polymer.

One special means of forming stereoregular polymers by free-radical mechanism is through the use of canal complexes. White and Brown (*16,17*) took advantage of the fact that canal complexes can be formed by various olefinic monomers with urea and thiorurea. These complexes form a crystal lattice, with the molecules of the monomers confined to the canals. The polymerization is started by brief exposure to a high-energy electron beam. Because the canals hold the molecules in a fixed position, the growing polymer chain could grow in only one way, resulting in stereospecific polymers prepared actually by a free-radical mechanism (see Figure 7-1).

White believes that it is possible that in these canal complexes of small flat molecules, the guest molecules are not lined up end to end but are actually packed in some sort of overlapping arrangement. He feels that it is even possible that the smallest molecules in this category, such as isobutylene and vinylidene chloride, might lie directly on top of each other as in a stack of coins. In either case, this sort of overlapping would greatly facilitate reaction between guest molecules.

Polymerization in the thiourea canal complexes yielded high-melting crystalline *trans* 1,4-addition polymers from 2,3-dimethylbutadiene, 2,3-

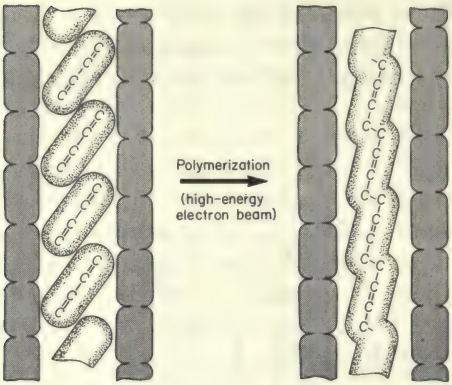


Figure 7-1. Illustration of polymerization in canal complexes.

dichlorobutadiene, 1,3-cyclohexadiene, and cyclohexadiene monoxide. Isobutylene and vinylidene chloride were also polymerized but yielded polymers that did not exhibit stereospecificity.

Crystalline polymers were also obtained from 1,3-butadiene (all *trans*-1,4), vinyl chloride, and acrylonitrite when urea canals were employed.

Ivanov and co-workers (*18*) reported application of this method to piperylene polymerizations. They failed to establish fully whether steric control was actually achieved, because they did not carry structure elucidation beyond infrared analysis.

7-2. Stereospecific Polymerization by Ionic Mechanism

As stated in Chapter 4, the influence of the counterion can have a stereoregulating effect on the incoming monomer. Bawn and Ledwith (*1*) point out, however, that the extent of this influence is not completely clear. The best insight into such problems comes from an approach which takes into consideration each ion pair as being able to exist in several distinct forms, depending upon the degree of separation. Such a separation was proposed by Winstein and Robinson, in that the ion pair can exist in four different forms (*19*):

$$\underset{\textit{covalent}}{RX} \rightleftharpoons \underset{\textit{intimate ion pair}}{R^{\oplus}X^{\ominus}} \rightleftharpoons \underset{\textit{solvated ion pair}}{R^{\oplus}\cdots(\text{solv.})X^{\ominus}} \rightleftharpoons \underset{\textit{free ions}}{R^{\oplus} + X^{\ominus}}$$

The degree of the dissociation of a particular species of ion pairs is, of course, a function of the nature of the components and of the solvent. And, as Bawn and Ledwith (*1*) also point out, because of the high reactivity of carbonium ions and carbanions, ionic polymerizations are necessarily performed in nonsolvolyzing, inert solvents. These solvents will, in many cases, preclude the formation of dissociated ions.

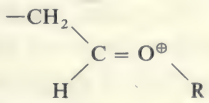
7-3. Steric Control in Cationic Polymerization

The first synthesis of isotactic polymers by ionic mechanism can be credited to Schildknecht et al. (*20*), who polymerized alkyl vinyl ethers cationically. When gaseous BF_3 catalyst was used to catalyze the polymerization of isobutyl vinyl ether in liquid propane at $-70°C$, an amorphous polymer resulted. However, when BF_3-ether complex was employed, a crystalline product formed. A number of crystalline polyvinyl ethers have been synthesized by this method (*21–23*).

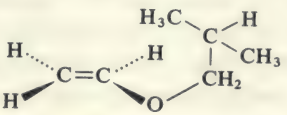
Originally it was assumed that the stereoregulating effect in these polymerizations was obtained from the heterogeneous nature of conditions used by Schildknecht et al. (*20*). Now it is known that crystalline polymers can be obtained in homogeneous conditions (*23*) as well. Also, the greatest amount of crystallinity was obtained at the lowest temperatures ($-70°C$), the crystallinity decreasing with an increase in reaction temperature. Here we find a similarity to steric control achieved by free-radical mechanism.

Within the last several years, a number of highly efficient catalytic systems evolved for formation of crystalline polyethers (*24*). As a result, much thought has gone into the mechanism that leads to stereospecificity, and various mechanisms have been proposed. Among these are mechanisms proposed by Cram and Kopecky (*10,11*), by Higashimura et al. (*25*), by Bawn and Ledwith (*1*), by Nakano et al. (*26*), and by others. Most workers, but not all, believe that because of the presence of a counterion near the terminal charged carbon atom, the electron configuration is sp^3 (tetrahedral) hybrid, rather than sp^2 (trigonal), particularly in solvents of low dielectric.

Bawn and Ledwith (*1*) point to nuclear magnetic resonance data obtained by Freeney et al. (*27*), which indicated only one form of mesomeric structure of alkyl vinyl ethers, presumably *trans*,



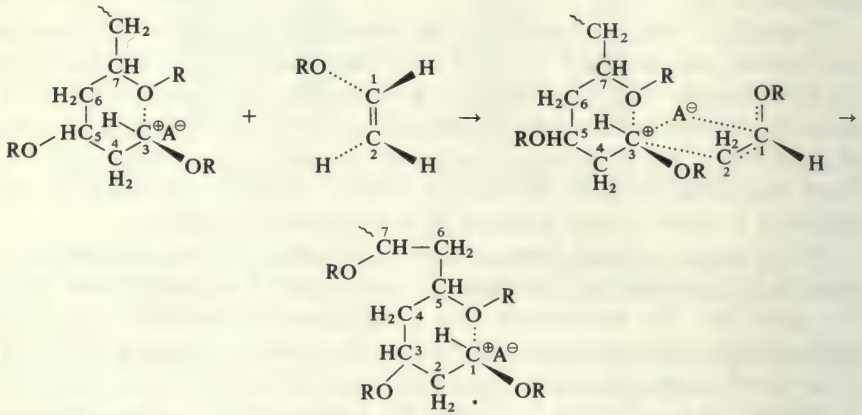
They reason that if such a form predominates, then an alkyl substituent containing at least three consecutive carbon atoms will cause steric blocking of one side of the olefinic bond,



The steric block shown above for isobutyl vinyl ether will be greatest for a neopentyl homolog but will decrease through isobutyl and *n*-propyl vinyl ether. No steric block should be possible for isopropyl and ethyl vinyl ether. Such an observation was made from molecular models. It correlates with experimental

findings, in that isopropyl vinyl ether fails to yield crystalline polymers but butyl vinyl ether does not.

So Bawn and Ledwith (*1*) postulate that in homogeneous polymerization the growing cation can be stabilized by a form of neighboring group interaction or intramolecular solvation through the oxygen atoms in the penultimate monomer unit (this would result in the formation of a four-membered ring) or, more probably, by formation of a six-membered ring with the oxygen atom of the last-but-three monomer unit,



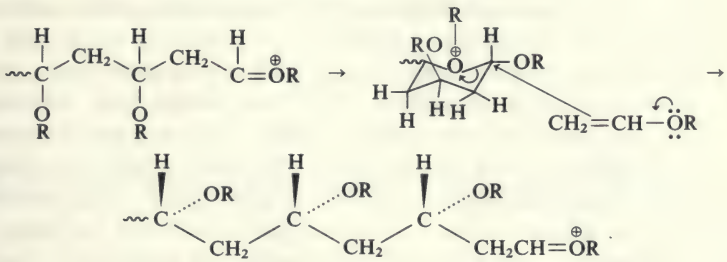
Such "backside" solvation or stabilization of the growing cation will lead to reactions at the cation involving an attack from the opposite side at the location of the counterion.

The Bawn and Ledwith mechanism is a form of an S_n2 attack with the retention of configuration. The configuration is maintained by the probable interaction of counterion $A^{\ominus}$ with both the existing and the newly forming carbonium ions in the transition state. This makes possible immediate intramolecular solvation of the newly formed carbonium ion on the same side as the original reacting carbonium ion was located. It might even be possible that solvation of the new cation occurs before it is completely formed, and in this manner the configuration of the growing carbonium ion is maintained throughout, provided the monomer molecules will enter as shown above (*1*).

Bawn and Ledwith admit, however, that their mechanism does not take into consideration the nature of counterion $A^{\ominus}$, although it can obviously exert an influence on both the rate and stereospecificity of the polymerization.

The Cram and Kopecky mechanism (*10*) differs in that it places much emphasis on the steric arrangements of the six-membered ring. Here it is suggested that the growing polymer chain occupies an equatorial arrangement to that of the —OR group attached to the growing end by virtue of its size, as it is larger than OR. When the monomer reacts with cyclic oxonium ion, the relative configurations of the first two asymmetric centers formed in each polymer chain will determine the overall configuration of that chain. Should

the configurations be similar, then the polymer chain will become isotactic, but if different, syndiotactic. A study of the molecular models indicates that in such cases isotactic placements are more likely,



The Cram and Kopecky mechanism fails to explain the influence of the various R groups on stereospecificity.

Furukawa investigated ionic polymerization of various polar monomers (*24*). He interprets the heterogeneous mechanism of stereoregular polymerization of vinyl ethers in terms of multicentered coordinations. This is based on the belief that in cationic polymerization, the coordination of polymer chains and monomers onto the catalyst would be possible if the complex counteranions have electrically positive centers. Thus in boron fluoride etherate anion, the boron atom would still have a positive formal charge, owing to the large difference in electronegativity between fluorine and boron. Coordination of alkylaluminum to the boron atom, as an example, would then be probable, eventually giving cation and coordinated counteranion,

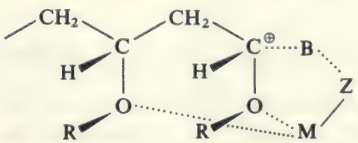
$$R_3Al + BF_3 \rightarrow [R_2Al]^{\oplus} + [BF_3R]^{\ominus}$$

The central metal in a counteranion of this type still carries a positive charge. Furukawa, therefore, points out that further coordination of alkylaluminum onto the anions is conceivable as long as the coordination number of the central atom is sufficiently large,

$$[BF_3R]^{\ominus} + AlR_3 \rightarrow [R_3Al \rightarrow BF_3R]^{\ominus}$$

The result is the formation of a complex counteranion enabling multicenter-coordinated polymerization.

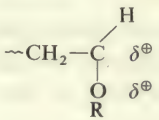
So, Furukawa proposes the following: Two neighboring ether oxygens which are linked to the polymer chain in the vicinity of the positively charged chain end are coordinated to the metal center of the complex anion. Monomer molecules then approach the growing chain only from the opposite side of that chain, thereby producing isotactic polymers exclusively (*24*),



A different explanation is offered by Nakano and co-workers (*26*), who studied various new catalysts that will give isotactic poly(vinyl isobutyl) ethers and in some cases isotactic poly(vinyl methyl) ether in reactions at room temperature. These were metal halides or their complexes, metal oxides and metal oxyhalides, organometallics combined with mineral acids, and metal sulfates combined with sulfuric acid. Among each one of these types, with the exception of the last one, there were catalysts that yielded both stereospecific polymers and also those lacking stereospecificity. All catalysts composed of metal sulfates combined with sulfuric acid, however, yielded stereospecific polymers. They concluded that a relationship appears to exist between the structures of these catalysts and the stereoregularities of the polymers. Thus tetrahedral compounds that have one active edge are particularly useful for preparing stereoregular polymers at room temperatures. In addition, Nakano and co-workers (*26*) observed that the shorter the length of the active edge, the more suitable the catalyst will be for stereospecific polymerization.

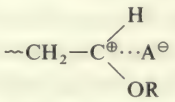
This led them to propose the following reaction mechanism. If the end of the growing chain,

is actually an sp^2 type of structure and not sp^3, as believed by others, then a vacant orbital on the terminal carbon atom of the growing polymer chain is in a state of resonance with the lone pair on the adjacent oxygen atom. The positive charge will, therefore, not be localized on the end carbon but will be distributed to the adjacent oxygen,

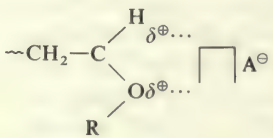


In such a picture, the electron density is estimated on the carbon atom at about 0.25 and on the oxygen at about 1.75, so that carbon is about +0.75 and oxygen about +0.25.

Then the combination of the end with counterion $A^{\ominus}$ is not of the type usually visualized,

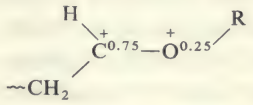


but rather

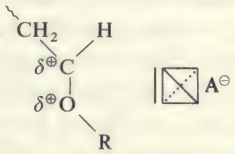


Here R is restricted to *cis* and *trans* forms, owing to resonance in the C—O bond, and is located in the plane opposite the CH_2 group, owing to steric hindrance.

Then the growing chain end should really be represented as

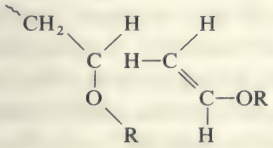


and the combination with the active edge of the counterion will be

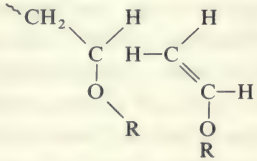


Now the monomer can add in four ways:

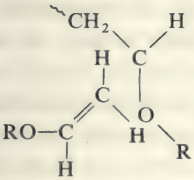
1.



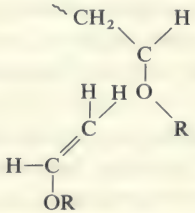
2.



3.



4.



Considering steric hindrance and mutual repulsion between substituents, the monomer should add by type-3 addition, thereby yielding an isotactic polymer (*26*).

They concluded that the less the number of active edges and the shorter their length, the more stable the counterion will be. So, one can summarize by saying that more work is needed to reach general agreement on reaction mechanisms of steric control in cationic polymerizations of vinyl ethers.

7-4. Steric Control in Anionic Polymerization

The original efforts in anionic polymerizations were not centered around the means for obtaining stereospecific polymers. Later, however, attention

has focused on use of anionic polymerizations to attain stereospecific styrene and its derivatives (*28–30*), as well as various acrylate esters (*31–33*), and N,N′-dialkylacrylamides (*34*). In all these reactions organometallic catalysts were employed, with best results coming from use of lithium alkyls and reasonably good results coming from Grignard reagents, dialkyl magnesium compounds, and sodium and potassium alkyls (*35,36*).

Glusker and co-workers (*37*) found that lithium alkyls were the most efficient catalysts for achieving steric control in anionic polymerization of α-methyl methacrylate from among many organometallic compounds, but only if low temperatures and hydrocarbon solvents were employed. Yet in the polymerizations of N,N′-dibutyl acrylamide with butyllithium initiator, isotactic polymers are obtained in good yields at room temperature (*35*).

Based on this observation, it was pointed out (*1*) that in anionic propagation, if the growing polymeric anions are almost free propagating species, then the requirements for stereospecific polymerization will be similar to those required to produce stereospecificity by free-radical mechanism. These, as mentioned, will normally be obtained only at very low temperatures. Furthermore, one should expect to obtain syndiotactic placement. This is supported by the fact that alkyllithium-initiated polymerizations of α-methyl methacrylate in 1,2-dimethoxyethane yield predominately syndiotactic polymers when carried out at about −60°C (*37*). Here reaction conditions favor the alkyllithium to be either a solvent-separated ion pair ($R^{\ominus}/\!/L_1^{\oplus}$) or free ions ($R^{\ominus} + L_1^{\oplus}$).

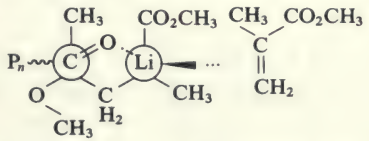
But, when reaction conditions favor the alkyllithium to be in the form of covalent ($R-L_1$) compounds or intimate ion pairs ($R^{\ominus}L_1^{\oplus}$) in essentially nonsolvating solvents such as aliphatic hydrocarbons, stereospecific polymerizations yield isotactic products like the polymerization of acrylic monomers.

The polymerization temperature here is a function of the monomer structure. Thus an *n*-butyl acrylate and methacrylate can be converted to isotactic polymers at room temperature in heptane (*31*). The same is true for N,N′-dibutyl acrylamide (*35*), but isopropyl acrylate, cyclohexyl acrylate, and methyl methacrylate have to be polymerized below −50°C to obtain isotactic polymers (*31,32*).

As shown, the reaction of alkyllithium with, say, methyl methacrylate is through the mechanism of complex formation or coordination between lithium atom and the π-electron system of the monomeric olefin (see Chapter 5). So, according to Bawn and Ledwith (*1*), once such a reaction has taken place, the growing polymeric alkyl lithium can be expected to have some enolic character, and, furthermore, the lithium atom can coordinate with the carbonyl oxygen of the penultimate monomer unit.

The cyclic intermediate can be regarded as involving intramolecular solvation of the lithium, and, owing to the intramolecular shielding that will occur on one side of the lithium atom, nucleophilic attack by the monomer molecule should occur on the opposite side, yielding a transition state analogous to S_N2.

When the bond-forming reaction between lithium and the incoming olefinic monomer takes place, the oxygen-lithium coordination link will rupture and the polymer anion will migrate simultaneously from the lithium to the methylene group of the monomer. The newly formed lithium enolate will then be immediately stabilized by intramolecular solvation, as previously. In this way the retention of configuration will be ensured, assuming the incoming monomer molecule always assumes the same configuration toward the lithium atom. An examination of molecular models shows that for methyl methacrylate, the configuration that involves the least steric interaction is the one in which the α-methyl groups is *trans* to the α-methyl group of the carbanion,

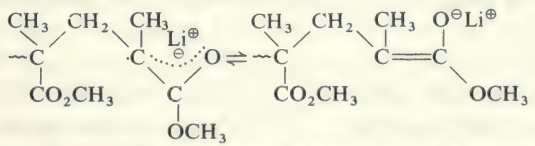


(The ester group and the polymer chain are always *trans* to each other.)

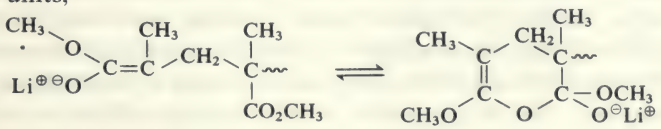
So, according to Bawn and Ledwith (*1*), in general, for stereospecific polymerizations that involve free-propagating species, the various approach configurations of the incoming monomers will differ only slightly in the amounts of steric repulsion or nonbonded interactions between the various substituent groups. As a result, the small differences in activation energy of the various modes of addition will usually be significant only at low temperatures.

In the case of the other acrylic esters, the bulkiness of the ester group might be found at the α-carbon, as in *t*-butyl acrylate or isopropyl acrylate. So the conformation of the incoming monomer may be governed by the bulkiness of the ester group, even though the same requirements as with methyl methacrylate should still be true, but this bulky ester group, will tend to shield one side of the double bond, causing the opposite side to be available to the lithium atom. This form of steric hindrance permits it to form isotactic polymers at 0°C (*31*).

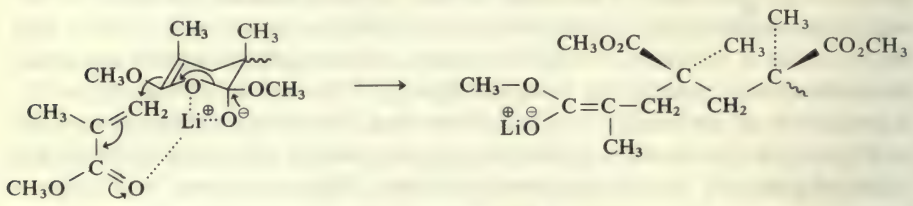
Cram and Kopecky (*10,11*) propose an explanation based on the belief that the growing lithium enolate has a complete alkoxide character,



This, they believe, is stablized by the formation of a six-membered ring, a product of an alkoxide attack on the carbonyl group of the penultimate monomer units,



Stereospecific propagation then proceeds by a Diels–Alder type of reaction (*38*), in which the six-membered ring is destroyed and a new ring made in one transformation,



So, according to Cram and Kopecky (*10,11*), stereoregulation is determined essentially by the ability of the lithium to coordinate simultaneously with two oxygen atoms. This will require that each monomer molecule approach the plane of the ring from below, in order to favor isotactic placement.

7-5. Anionic Polymerization of Dienes

Stereospecific anionic polymerization of the dienes follows essentially the same type of chemistry as that of the acrylic esters. Lithium alkyls, which are soluble in hydrocarbon solvents and in which they will also disassociate, cause the polymer formation under homogeneous conditions. On the other hand, the salt-like organic compounds of alkali metals such as sodium or potassium are insoluble and the reactions are therefore carried out under heterogeneous conditions.

Polyisoprene with more than 90% 1,4-*cis* structures can be obtained in hydrocarbons with organolithium using homogeneous conditions. In polar solvents, however, both lithium and other alkali alkyls will yield polyisoprenes that are predominately 1,2-; 3,4-; and 1,4-*trans* structures.

Sinn and Potat (*39*) explain the stereoregulation that occurs in nonpolar solvent on the basis of reaction of the alkyllithium with isoprene. They point to the formation of poly(isopropenyl lithium) in the initiation step of the polymerization,

$$\text{Li—R} + \text{CH}_2\text{=CH—CCH}_3\text{=CH}_2 \rightarrow \text{Li(CH}_2\text{—CH=CCH}_3\text{—CH}_2\text{)R}$$

$$\text{Li(CH}_2\text{—CH=CCH}_3\text{—CH}_2\text{)}_n\text{—R} + \text{CH}_2\text{=CH—CCH}_3\text{=CH}_2 \rightarrow$$

$$\text{Li(CH}_2\text{—CH=CCH}_3\text{—CH}_2\text{)}_{n+1}\text{—R}$$

The further insertion of isoprene between the alkenyl radical and lithium atom does not change the alkenyllithium structure, thereby preserving the reactivity of the Li—C bond. They draw a diagram of various configurations in relation to their entropies of activation based on consideration of the frequency factors for the various poly reactions of isoprene with the organolithium compounds.

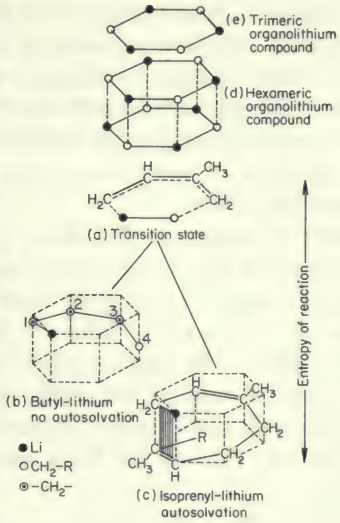


Figure 7-2. Possible structures of associated organolithium compounds, the adduct of organolithium compounds and isoprene, the monomeric form of butyllithium, and the autosolvated monomeric form of polyisoprenyllithium. (Courtesy of *Angewandte Chemie*.)

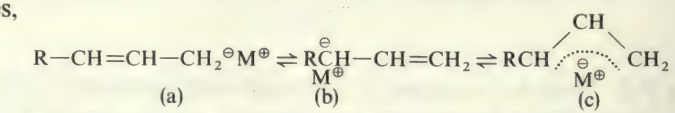
This is shown in Fig. 7-2. Comparison of the structures demonstrates that in case (c) the interaction between the (d), (e) double bond and the Li—C bond in the poly(isopropenyl lithium) requires fixation of the carbon chain and thus a loss of degrees of freedom. Sinn and Potat (*39*) confirmed such a relationship with kinetic studies and by infrared analysis. This suggests again that structural relationships should play a far smaller role in reactions taking place in polar solvents such as ether than they would in hydrocarbons.

Experimental evidence was presented earlier by Kuntz and Gerber, who studied butadiene polymerizations with butyllithium in heptane (*40*). They found that the reaction yields a product that is approximately equal in amounts of *cis*-1,4 and *trans*-1,4 and contains about 10% 1,2 adduct. The composition of the product was found to be independent of both catalyst and monomer concentrations. Small amounts of ether, however, changed the product composition, increasing the amount of 1,2 adduct. In tetrahydrofuran as the solvent, the product was 80% 1,2 adduct, with only a small amount of *cis* and *trans* 1,4 addition.

The same is true of isoprene polymerizations initiated by lithium or alkyllithium in hydrocarbon solvents. The reactions will yield a high amount of *cis*-1,4 polymer, the product being the result of stepwise growth of an essentially covalent or intimate-ion-pair lithium-carbon bond. This was discussed in Chapter 5.

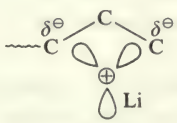
When the lithium-initiated polymerizations are performed in solvating or basic solvents, however, such as in the presence of ethers or even amines, the resulting polyisoprene contains mainly 3,4 linkages with about 25% *trans*-1,4 adduct. Significantly similar structures result when the polymerizations are initiated by other alkali metals, even in hydrocarbon solvents. And again this can be rationalized on the basis of the relative ionic radii and ionic character in the alkali-metal organoderivatives.

Thus the organometallic compounds of sodium, potassium, rubidium, and cesium will be much more polar and much more dissociated than their lithium analogs. Bawn and Ledwith suggest (*1*) that the basic structures of these metal alkyls approximate, even in hydrocarbon solvents, the solvent-separated ion-pair structure for lithium alkyls. The catalyst reacts essentially as the solvated anion, and in diene polymerization as the allylic anion. They compare the behavior of this allylic anion to that of allyl Grignard reagents (*41*) and point to the significance of the fact that of the three extreme structures for such derivatives,

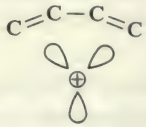


the reaction with carbonyl compounds (*42*) yields products derived from (b). Now, the polymerization of isoprene with the corresponding organometallic derivatives also yields mainly 3,4 adduct, indicating that the growing allyl metal derivative also reacts as if it had an analogous structure.

O'Driscoll et al. (*43*) proposed a mechanism for homogeneous anionic polymerization of dienes that goes somewhat further in explaining what is taking place in stereospecific anionic polymerization. They point out that the metal counterion exists in close proximity to the propagating chain end. And they propose that here as in a propagating poly(styryl carbanion) (*44*) the terminal charge end is complexed with the metal cation through the occupied π-orbitals of the chain end and the unoccupied 2 orbital of the lithium ion. Similar complexing with the monomer is assumed to take place in the transition state. In the case of the dienes (*44*) they follow a suggestion by Kennedy and Langer (*45*) and consider $Li^{\oplus}$ to be hydridized to a tetrahedral sp^3 configuration with four vacant orbitals. They also recognize the bidentate nature of the allylic anion chain end and of the diene monomer. This complex of $Li^{\oplus}$ with the allylic chain end and with the diene monomer they show as follows:



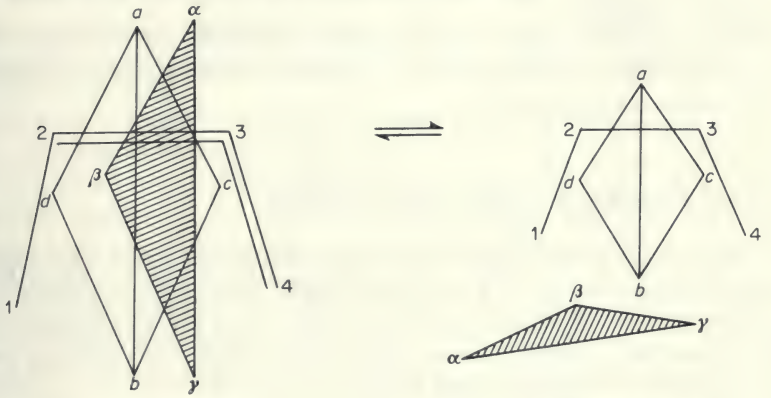
allylic chain and anion



diene monomer

In the propagation step, both monomer and chain end complex with the same counterion, giving rise to the spatial configuration shown below. There the

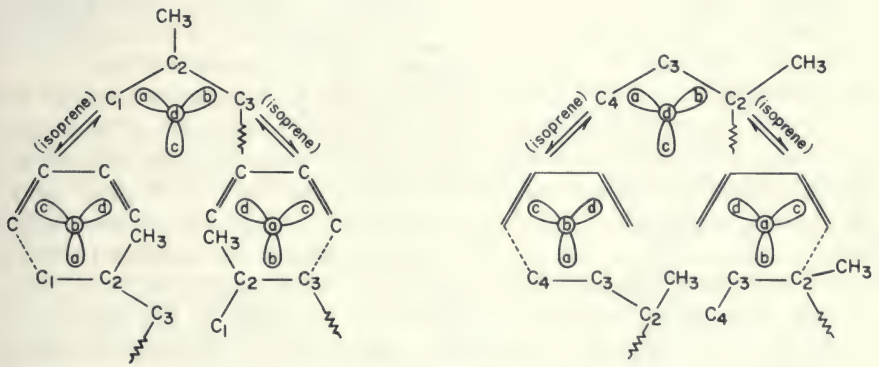
$Li^{\oplus}$ is represented by the tetrahedron *abcd*, the allylic chain end by the triangular plane (parallel to plane *abc*), and the monomer by the plane 1234 (parallel to plane *bcd*). In the transition state the allylic plane is considered to have moved relative to the counterion and monomer, so that it is now parallel to the plane of the monomer and somewhat below it:



ground state *transition state*

When the asymmetrically substituted isoprene is polymerized, various reactions are possible, because the monomer can add to the chain end through either C_4 or C_1, giving rise to isomers. Each case can pass through two transition states. Transition states I_1 and I'_1 will give 1,4 adducts and I_2 will give 3,4 adducts, while I'_2 will give 1,2 adducts.

I *I′*



I_1 I_2 I'_1 I'_2

In the case of hydrocarbon solvents the complex would be tight, and they assume that the methyl group will sterically hinder rotation of the $C_2—C_3$ bond and so constrain the 1,4 addition to a *cis* configuration. In the presence of a

strong solvating agent, such as tetrahydrofuran, the complex would be looser and then thermodynamically favored *trans* addition would take place.

They point out that with large counterions, such as sodium or potassium, the larger size would give rise to looser complexes. As result polymers are formed in hydrocarbon solvents which are similar to those produced with lithium in tetrahydrofuran.

O'Driscoll and co-workers (*44*) tested their proposed mechanism by interpreting it quantum mechanically and obtained semiquantitative agreement with their experimental results.

7-6. Steric Control with Ziegler–Natta Catalysts

The large appeal of the Ziegler–Natta catalysis is the steric control it is usually possible to achieve. Actually the original Ziegler discovery was specific to the polymerization of ethylene, and it was Natta and his collaborators who developed similar catalytic systems useful in the preparation of many stereoregular polymers of high molecular weight.

Most mechanisms proposed to explain the reaction concentrate on the chemical nature of initiation and propagation steps without explaining what actually leads to the steric controls. These mechanisms were discussed in Chapter 6. Because, more often than not, the catalysts are heterogeneous in nature, it is often assumed that steric controls are achieved as a result of the heterogeneity of these systems, and it is generally agreed that the surface of the heterogeneous catalyst does play a large part in controlling the stereochemistry of the propagation.

Natta (*46*) demonstrated that crystal size and type of reduced transition-metal halide, and the reducing agent, play a very important part in controlling the reaction rate, molecular weight of the product, and the stereochemistry.

Stereospecific control was shown, however, with homogeneous catalysts as well. McIntosh et al. (*47*) studied the stereospecific polymerization of butadiene using cobaltous chloride with triethylaluminum and with aluminum chloride as catalysts in benzene solvent. They were primarily concerned with the effect aging of the catalyst (taking place over a period of nearly 2 years) has on the stereospecificity of the product. The freshly prepared catalyst appeared as a straw-yellow liquid over black insoluble solids. Within a few weeks they noted that a separate liquid phase formed at the bottom of the catalyst. The amount of the dark lower layer increased on standing until all the solids dissolved. Polymers prepared from the upper layer of the catalyst showed decreased percentages of *cis* double bond as the catalyst aged, an effect that was linear up to approximately 1 year. From 1 to 2 years, however, the upper layer yielded polymers that were essentially constant in composition, possessing 70% *cis* olefinic bonds. On the other hand, the dark lower layer yielded polymers which were greater than 95% *cis* over the entire 2-year period of their study.

In addition, they found that the clear upper layer of the catalyst retained its stereospecificity with age if stored in the absence of undissolved solids, this being apparently a case of steric control under homogeneous conditions.

It may be observed, generally, that major investigations of the influence of catalyst structure on stereospecificity of the resultant polymer have, to date, been conducted on propylene. Nevertheless, most α-olefins (straight and branched-chain), as well as styrene and its substituents, have by now also been investigated. Cooper summarized the properties of these various materials in a review article (*48*).

As stated in Chapter 2, differences in the properties of various steric forms of polymers are quite enormous. The result of regularity in steric arrangement is the ability of the chains to pack together into ordered three-dimensional crystal structures. Natta and Corradini (*49b*) demonstrated that isotactic polymers can form only helix-type crystalline structures, whereas syndiotactic polymers can form either helical or planar structures.

The isotactic polymers are the *cis* isomers of head-to-tail adducts of vinyl polymers. The syndiotactic polymers are the *trans* isomers. In the isotactic polymers of olefins possessing bulky side groups, steric hindrance forces the helixes to be looser and to have a greater pitch than in isotactic polypropylene. Most of the stereospecific polar polymers also tend to adopt a helical conformation in the crystalline state. The melting points of some of these are given in Table 7-1.

Danusso comments (*49a*) that combinations of trivalent titanium halide with organometallic aluminum compounds are actually the typical heterogeneous catalysts that are stereospecific for the whole class of the aliphatic α-olefins but not those of tetravalent titanium halide. In some cases completely stereoregular polymers can be obtained with some monomers and a very high degree of isotacticity with others (*50*).

TABLE 7-1
Some Stereospecific Polymers

Polymer	Structure	m.p.	Ref.
Polyacetaldehyde	Isotactic	165	*49c*
Poly(butyl acrylate)	Isotactic	82	*33*
Poly(*i*-butyl vinyl ether)	Isotactic	165	*21*
Poly(*N*-isopropylacrylamide)	Syndiotactic	170–200	[a]
Poly(*NN*-diisopropylacrylamide)	Isotactic	350	*35*
Poly(methyl methacrylate)	Isotactic	150–160	*38*
	Syndiotactic	190–200	*38*
Polypropionaldehyde	Isotactic	165	*1*
Poly(propylene oxide)	Isotactic	72–75	[b]

[a] D. J. Shields and H. W. Coover, Jr., *J. Polymer Sci.*, **39**, 532 (1959).
[b] G. Natta, P. Corradini, and G. Dall'Asta, *Atti Accad. Nazl. Lincei, Rend.*, **8**, 408 (1956).

$TiCl_3$ itself is a solid, crystalline, and polymorphous material with four crystalline modifications: α, β, γ, and δ (*51*). The β modification, brown in color, yields catalysts of only limited stereospecificity toward α-olefins. The other three crystal forms are violet in color and all yield stereospecific polymers. Danusso (*49a*) feels that this must be related to the structural peculiarities in the crystal lattice which becomes the support for the catalytically active centers formed by $TiCl_3$, located on the surface and reacting with the organometallic compound.

From the study of the α, γ, and δ forms of $TiCl_3$, Natta and co-workers (*50*) concluded that the various differences peculiar to the three crystal forms are not as significant in the stereospecific behavior of the catalysts as is the nature of the organometallic reagent used.

Natta's group (*49*) studied the effect on the stereospecific activity of the violet $TiCl_3$ catalyst with various organoaluminum compounds. These compounds were employed in their pure state and also complexed with different substances, generally Lewis bases. The compounds were of the general type Et_2AlX, where Et is the ethyl group and X could be another ethyl group, a halogen, an alkoxy group, a similar group but with sulfur or selenium in place of oxygen, or even a complex group containing nitrogen, such as a piperidyl.

They found that the highest catalytic activity was possessed by catalysts prepared from triethylaluminum followed by diethylaluminum monohalides. The others showed less activity and in some cases no reactions resulted. But the stereospecificity remained high, although dependent on the nature of the organometallic compound used. The analysis of the results led to the conclusion that the formation of catalysts takes place only if there is in solution a sufficient concentration of the monomeric species of the organometallic compound, and that therefore it is the last one which is responsible for the formation of the active centers on $TiCl_3$. This conclusion also coincides with the fact of a previous observation (*52*)—that certain catalysts can be stereospecifically inactive at low temperature but become active when used or even only prepared at a higher temperature.

Within the last several years Natta and co-workers investigated the copolymerization of ethylene with *cis*-butene-2 and *trans*-butene-2 (*53,54*) with pentene-2 (*55*), with cyclopentene (*56*), with cyclohexene (*56*), with cycloheptene (*57*), and with *cis*-cyclooctene (*58*). Here the catalysts were prepared from reactions of vanadium salts with organometallic aluminum compounds. In these reactions, the cycloolefins were inserted into the chains by the mechanism of double bond opening, keeping the cyclic structure. It was noted that in this copolymerization of the cyclic monomers with ethylene, the rings possessing an odd number of carbon atoms exhibited greater reactivity. Furthermore, at least in the case of butene-2, the activity was markedly greater with the *cis* isomer. The more active monomers yielded alternating copolymers which were stereoregular (*59*).

X-ray diagrams demonstrated erythrodiisotactic arrangement (see Figure 7-3).

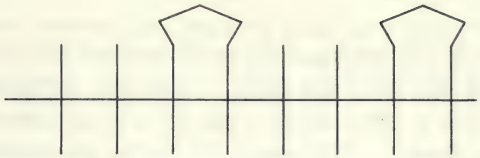


Figure 7-3. Illustration of the erythrodiisotactic arrangement of the copolymer.

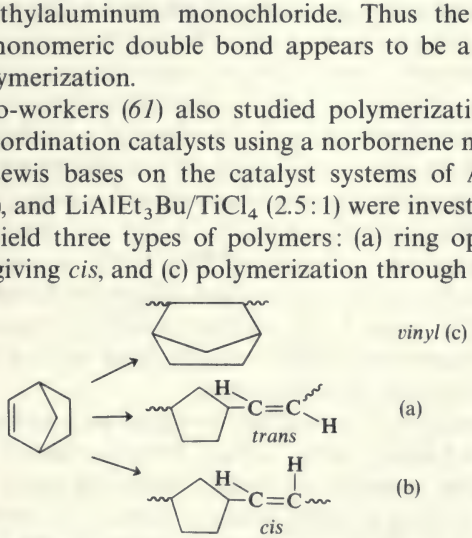
The odd-carbon-number cycloolefins show a symmetry plane normal to the double bond. In these olefins, the ring atoms, which did not lie in the reference plane, were all placed on the same side of it. Such molecular geometry allows a free approach of an attacking reagent at one side of the double bond even when cumbersome in size. The conclusion would be that such a polymerization should lead to *cis* isomers.

This mode of attack on the double bond, however, would not be favored in a ring having an even number of carbon atoms.

It is significant that Natta and co-workers have also observed (*60*) a repetitive *cis* opening in the preparation of diisotactic polymers from alkenyl ethers and β-chloro vinyl ethers with homogeneous coordinated catalysts.

Danusso concludes (*49a*) that the reactivities of those olefins possessing internal double bonds with heterogeneous catalysts are actually similar to reactivities with homogeneous catalysts, at least when using vanadium acetylacetone and diethylaluminum monochloride. Thus the *cis*-type repetitive opening of the monomeric double bond appears to be a general fact in the coordination polymerization.

Tsujino and co-workers (*61*) also studied polymerization of cyclic olefins with the aid of coordination catalysts using a norbornene monomer. The effect of addition of Lewis bases on the catalyst systems of $AlEt_3/TiCl_4$ (2.5:1), $AlEt_3/TiCl_4$ (1:1), and $LiAlEt_3Bu/TiCl_4$ (2.5:1) were investigated. Norbornene can potentially yield three types of polymers: (a) ring opening giving *trans*, (b) ring opening giving *cis*, and (c) polymerization through the double bond:



The catalysts used ordinarily gave polymers that were a mixture of (a) and (c) or (a) and (c), respectively. Addition of Lewis bases, however, caused formation of high-molecular-weight polymers which were exclusively either (a) or (b).

7-7. Stereospecific Polymerization of Cyclic Ethers

As mentioned, cyclic ethers can be polymerized by both cationic and anionic mechanism as well as by coordination catalysis. In spite of that, stereospecific

polymerization of propylene oxide probably has received most of the attention to date. Recently it was disclosed by Price and Spector (*62*) that the epoxide polymerization by the three mechanisms proceeds exclusively with inversion of the configuration at the carbon atom of the ring undergoing attack. In a subsequent paper, Price and Spector (*63*) reported an extension of these stereochemical studies to the polymerication of *cis* and *trans* isomers of 1,2-dideuteroethylene oxide. They carried out these polymerizations using an anionic initiator (*64*), a cationic initiator prepared from triethylaluminum and water (*65*), and two coordination catalysts, diethyl zinc–water (*66*) and ferric chloride–propylene oxide (*67*).

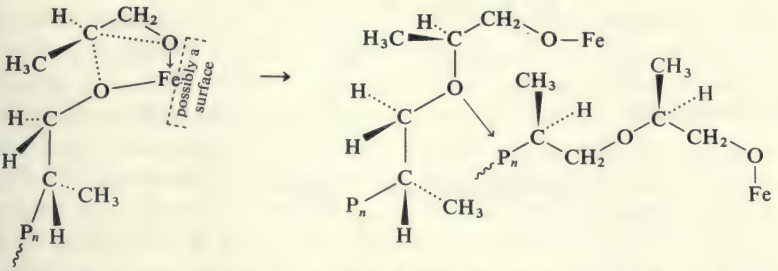
A spectroscopic study of dry films made from their products revealed that two distinctly different spectra were obtained, depending on the stereochemistry of the monomer and regardless of the nature of the catalyst used. At the same time, solution spectras of their products were undistinguishable. This difference they explained to be due to the different interactions of the C—H and CH_2 modes of the *meso* and *dl* configurations in the fixed geometry of the crystalline state.

Price and Spector concluded that on the basis of the established inversion occurring for S_n2 (base) ring opening of epoxides, all ring-opening polymerizations (so far studied) proceed by inversion of the configuration. In addition, their own data indicate that *cis*-dideutero ethylene oxide polymerizes to units that are exclusively *dl*, and *trans* to units that are exclusively *meso*.

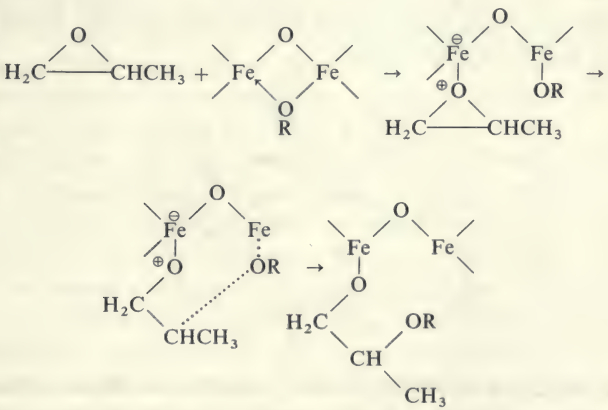
Pruitt and Baggett (*66*) were the first to report stereospecific polymerization of propylene oxide with the aid of ferric chloride or ferric hydroxide catalysts. The crystalline product was shown to be isotactic polypropylene oxide. This work was extended by Price and Osgan (*67*) to the preparation of optically active (−) propylene oxide monomer which was polymerized with KOH catalyst to an optically active polymer melting at 55.5–56.5°C. However, when a racemate propylene oxide was polymerized with KOH, a syrupy liquid resulted. But, when the optically active (−) propylene oxide or its racemate were polymerized in ether at 80°C using $FeCl_3$ catalyst, essentially similar products were obtained in both cases, except that the crystalline regions from the optically active monomer were also optically active.

Price and Osgan (*67*) believe that stereoregular polymerization of propylene oxide proceeds at a heterogeneous surface. They concluded, therefore, that the product can be either isotactic or atactic, depending upon whether the ferric alkoxide bond is part of a heterogeneous surface or whether the system is homogeneous. What usually occurs is that a mixture of both is present in the reaction. So they proposed [a very similar suggestion was also made by Cram and Kopecky (*10*)] that stereoregularity is explained by assuming that in the transition state the bulkiness of the growing chain is greater than the CH_3 group in propylene oxide or than the proton. The surface causes the transition state to be more compressed and also causes steric repulsion between the incoming monomer and the terminal unit in the chain to be minimized by forcing the

methyl substituent to be *trans* to the methyl group of the penultimate unit. Such a conformation will also ensure that steric repulsion between the in-coming monomer and the large bulky growing polymer (P_n) be at a minimum,



Colclough et al. (*68*) point out that ferric alkoxides are highly associated in nonpolar solvents and that the catalyst would, therefore, be a simple ferric alkoxide in structure. Water addition has a stereoregularity-producing effect which may be a direct result of increased association after partial hydrolysis of the ferric compound. Also, Gee demonstrated (*69*) that ferric alkoxide catalyst can be made highly stereospecific by partial hydrolysis and yet still remain in solution during polymerization, indicating that the active catalyst still contains Fe—O—Fe bonds. Based on this idea, Bawn and Ledwith (*1*) show the polymerization as follows:

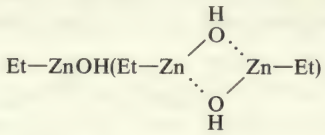


The *cis* opening of the epoxide ring would be made certain by the forces of interaction between iron atoms and the various oxygen atoms as shown. The above mechanism involves a type of S_n2 reaction on the ferric alkoxide so that, as with the methyl methacrylate and isobutyl vinyl ether shown earlier, there will be increased restrictions on the conformation of the in-going monomer unit when it approaches the reaction cite.

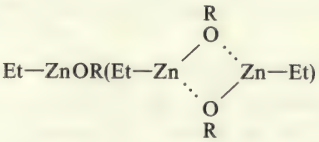
Furukawa (*24*) also carried out polymerization of propylene oxide using diethylzinc activated by a controlled amount of water or alcohol as catalyst.

He pictures these catalysts as follows:

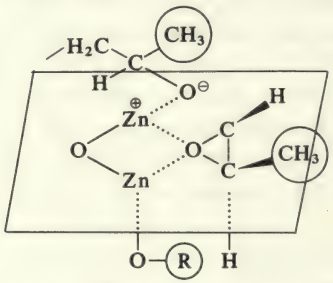
$Et_2Zn—H_2O$ system:



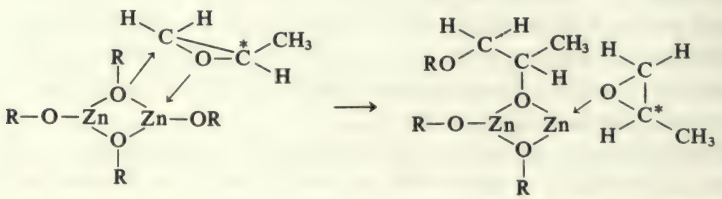
$Et_2Zn—ROH$ system:



The studies indicated that an alkoxyl group in the catalyst plays an influential role on stereoregulation in such propylene oxide polymerizations. This was particularly true of *n*-butyl and lower alcohols. In addition, an optically active polymer was formed from DL-propylene oxide, using optically active alcohols as cocatalysts. It was interesting that $[\alpha]_D$ changed in sign in different solvents, an effect originally reported by Price and Spector (*63*). Furukawa speculates that asymmetric induction might be occurring either through direct stereoregulation by an alkoxyl group in the catalyst or through indirect regulation due to the successive interaction between the monomer and the penultimate unit in the growing polymer chain. He draws the possible arrangement of monomer units in which a key atom for stereoregularity would exist in the monomer but not in the chain end:



Tsuruta et al. (*70*), who worked with Furukawa on these syntheses, feel that the polymerization is initiated by the coordination of propylene oxide onto the catalyst,



Furukawa also carried out studies (*24*) on catalytic systems useful for the polymerization of four-, five-, and six-membered cyclic ethers, and on copolymers of two cyclic ethers of different ring sizes, including six-membered cyclic ethers. He did not report, however, whether these polymers possessed any steric regularity. Furukawa and co-workers also investigated the formation of an optically active polymer from benzofuran by use of asymmetric induction (*71*). They came to feel that their theoretical conclusions about the mechanism reached earlier (*72*) were correct, in that the orienting effect of the asymmetric initiation, if any, actually decays rapidly with increasing polymer length. The asymmetric propagation, on the other hand, can allow the embedded monomer units to select one of the possible asymmetric configurations with a specific probability at each step of the chain growth. Thus the optical activity of polybenzofuran obtained with catalytic system $AlCl_3$:EtSnCl:M*OSnEt [where M* is (−) menthol] must be attributed to the prevalence of monomeric units having a specific configuration in the polymer chain and not to the activity of the initiator.

7-8. Stereospecific Carbonyl Polymerization

It should be easy to visualize that just as one can form an isotactic polypropylene, or an isotactic poly(propylene oxide), one should be able to form an isotactic polyacetaldehyde, and, of course, the same reasoning should apply to the syndiotactic analogs, to polymers of ketones, and so on.

Much work has gone into polymerization of aldehydes other than formaldehyde (*1*). The original polymers of acetaldehyde were amorphous, but since then Furukawa and co-workers prepared crystalline polymers by using activated aluminum as the catalyst at −80°C (*73*).

Novak and Whaley reported crystalline polymers from butyraldehyde and heptaldehyde by using very high pressures and cationic catalysts (*74*).

By using anionic initiators Natta and co-workers (*75*), Furukawa and co-workers (*76*), and Vogl (*77*) prepared crystalline polymers by polymerizing aldehydes in the presence of organometallic compounds. Specifically, trialkylaluminum or triarylaluminum in toluene or heptane yielded crystalline polymers from acetaldehyde, heptaldehyde, and propionaldehyde at −80°C. These polymers were all isotactic, forming a fourfold helical conformation. Furukawa et al. (*73*, *76*) also demonstrated that stereoblock and crystalline polymers of various aldehydes can be formed when aluminum oxide is activated by metal alkyls such as diethyl zinc. The crystalline polyacetaldehyde prepared by Vogl (*77*) with lithium alkoxide was insoluble in common solvents and melted at 165°C.

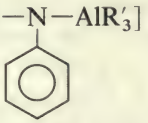
To polymerize acetone to a crystalline polymer Furukawa (*24*) used a modified Ziegler catalyst, consisting of triethylaluminum, titanium tri- or tetrachloride, and a metal salt, such as calcium chloride, sodium acetate, or magnesium acetate. He found the last component essential for acetone polymerization. A

similar procedure also yielded block copolymers of acetaldehyde and propylene.

The stereospecific polymerization of acetaldehyde was the subject of investigation by other research groups as well (*78–81*). The group, headed by Tani (*79–80*), has developed organometallic catalysts that can be ascribed the general formula

$$M[R_2AlOAlR'_3]$$

as well as an analogous system in which an N-phenyl group replaces the oxygen (*82*)



These compounds are formed through a reaction of a toluene solution of R_2AlOLi (a Lewis base) with toluene solution of AlR_3 (which acts as a Lewis acid). This leads to a crystallizable complex of the above structure. The R is an ethyl and R′ isobutyl or methyl group. Both types of catalysts yield polyacetaldehyde at $-78°C$, of which above 80% is isotactic.

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8

Bulk, Solution, Suspension, and Emulsion Polymerization

Many different techniques are employed for preparing macromolecules. Most of these can be divided into four methods: polymerization in bulk, in solution, in suspension, and in emulsion. The bulk, or mass, polymerization technique is useful in both addition and condensation polymerizations. To a certain extent this is also true of solution polymerizations. Suspension and emulsion techniques are mainly used in addition polymerizations, primarily for free-radical reactions. Ionic-type addition polymerizations are usually, but not always, conducted in solution.

8-1. Bulk Polymerization

Addition bulk polymerizations represent the simplest of all polymerization systems. These are characterized by their initial homogeneity and consist of carrying out the reactions on the monomers alone with or without added initiators or other materials. Once polymerization is initiated, mass-type polymerizations may exhibit two types of behavior.

System A. Polymer is soluble in monomer at all stages of conversion. Here there is no question about initiation occurring in the monomer, because the system contains nothing but monomer and initiator (if it is used). A monomer-soluble initiator would be used. If the polymerization is initiated thermally or with ultraviolet light, then of course nothing except the monomer is present. As the polymerization progresses, the viscosity increases noticeably, and the propagation takes place in a medium of associated polymer chains dissolved in, or swollen by, the monomer until the monomer is consumed. Termination in a free-radical bulk polymerization can occur in two ways: by the combination of two growing chains or by chain transferring.

System B. Polymer is insoluble in the monomer. In this system, initiation also must occur in the monomer. Precipitation of the polymer occurs without observable increase in solution viscosity. Vinylidene chloride and acrylonitrite

are good examples of such monomers, as they are not solvents for their corresponding polymers. Such systems have an activation energy similar to that of a mass polymerization. The rates are initially proportional to the square root of the catalyst concentration. The molecular weights of the formed polymers are inversely proportional to polymerization temperatures and to catalyst concentrations.

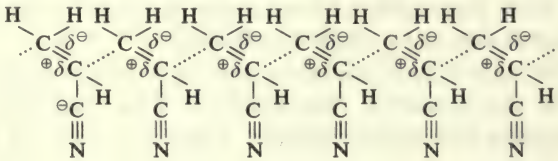
The molecular weights of the formed polymers far exceed their solubility limits in the monomers. For example, acrylonitrite monomer is not a solvent for polyacrylonitrite of a molecular weight of 10,000, yet polymers of molecular weights as high as 1,000,000 were obtained by mass free-radical polymerizations of this monomer. The conclusion is that propagation of polymerization must occur in the swollen precipitated polymer particles. Otherwise the molecular weights of the formed polymers would have been limited to the maximum molecular weight at which the polymer will remain in solution in the monomer, prior to precipitation. Then the rate and not the molecular weight would have been controlled by catalyst concentrations.

A special type of addition bulk polymerization involves a technique which was developed recently and which is based on polymerizing olefins or cyclic monomers by means of radiation in the solid state. The reaction is carried out at a very low temperature, well below the melting temperature of the monomers. Ionizing radiation is used to initiate the reaction. The conversion proceeds very rapidly, the reaction being completed in a few seconds or less. The advantages of this method are speed and (often) steric control.

Semenov (*1*) suggested that what is happening is that the highly excited monomers produced by this high-energy initiation attack adjacent monomers in their crystal lattice successively, step by step, thereby causing the polymers to grow. He postulated that the heat of polymerization released in the propagation could possibly excite the end of the growing chain electronically. Magat (*2*) also pointed out that polymerization at these extremely low temperatures may well proceed by an electronic excitation of the crystalline aggregates of the monomers.

If we assume that the polymerization follows the crystal lattice, then the crystal geometry of the monomer will be important in a polymerization of this type. Sobue and co-workers (*3*) propose a reaction mechanism for such polymerizations, which they term *electronic polymerization* [Tabata et al. (*4*)]. They postulate the collective excitation of a number of monomer units as a whole by the incident high-energy beam, thereby instantly changing the whole unit to a polymer.

They show an excited unit of acrylonitrite as follows:



Low activation energy in such solid state polymerization tends to support the above mechanism.

In any event, these solid state polymerizations appear to be controlled by the crystal structure of the monomer and, as a result, often yield highly stereospecific polymers.

As shown in Chapter 5, bulk-polymerization techniques can be applied to ionic addition polymerizations as well. For example, tetrahydrofuran can be polymerized in bulk with Lewis acids. The big disadvantage of bulk polymerization, by the free-radical and especially by the ionic mechanism, is that one has to overcome reaction exotherms, particularly if these reactions are conducted on a large scale.

8-2. Solution Polymerization

Solution polymerization may be looked upon as mass polymerization in which the monomers are soluble to varying degrees in added solvents. The solvents may be (1) complete solvents for the polymers, (2) partial solvents, or (3) nonsolvents for the polymers.

Case A. Monomer and polymer are both soluble. Such systems can be represented by the free-radical polymerization of styrene in benzene or toluene. Initiation and propagation occur in the oil phase. According to the mass-action law, the rate of polymerization is lower than in mass polymerization, and with increase in dilution, the rate and the molecular weight of the polymer are decreased. The presence of nonpolymerizable solvent means that kinetic chain transferring can occur more frequently with increased dilution. If the solvent is active as a telomer or retarder, it combines with growing chains. In such a reaction solvent-soluble catalysts are preferred.

Case B. Monomer is soluble in solvent, but polymer is only partially soluble or completely insoluble. Here, too, initiation occurs in the oil phase. As polymerization progresses, there is some increase in viscosity with conversion, followed by precipitation. Now the precipitated polymer chains are swollen by diffused and absorbed monomer and further propagation and termination occurs in these swollen particles. As in case A, the presence of a solvent increases the probability of chain transferring; and if the solvent is active as a telomer, it tends to combine with the growing chain. This, in other words, is similar to an increase in viscosity with conversions, but is further complicated by the presence of solvent molecules.

Free-radical polymerization of vinyl chloride in benzene and of acrylonitrite in chloroform or benzene can be used as examples of such cases. Polyacrylonitrile is insoluble in chloroform in molecular-weight ranges beyond 5000 to 6000; yet when acrylonitrite is polymerized in chloroform, molecular weights in excess of 50,000 (with attached telomerized chlorine atoms) are achieved. This can only be explained on the basis that both monomer and chloroform were absorbed by, or diffused into, the low-molecular-weight swollen polymer

chains during their growth. Jenckel and Suss (*5*) polymerized styrene in benzene (in which the polymer is soluble) and in ethyl alcohol (in which the polymer is insoluble). The average molecular weights obtained are given in Table 8-1.

These results indicate that the molecular weight of the polymer is not lowered in a solution polymerization in which a polymer precipitates, provided the solvent used does not possess high telomerizing activity.

Case C. Monomer is partially soluble in solvent and polymer is completely insoluble in solvent. The best example of such a solvent would be water. Some monomers, such as styrene, are only slightly soluble in water, others, such as vinyl acetate and acrylonitrite, are soluble, up to 5–7% at room temperature. If an aqueous saturated solution of acrylonitrite is polymerized in the presence of a water-soluble free-radical catalyst, the system behaves initially as in solution polymerization. The resultant molecular weight and the rate of reaction are lower than are obtained by polymerization in bulk. The polymer will precipitate. Yet, in the system described here, molecular weights *in excess of 50,000* are easily formed.

Free-radical solution polymerizations such as case A can actually be carried out in two ways. One way is to conduct the reaction in the same manner as is done with so many other organic reactions that are carried out in solution. The monomer is dissolved in a solvent, the initiator added, and while the reaction is stirred under an inert atmosphere, heat is applied for a given period of time to achieve conversion. Many examples of such polymerizations of vinyl monomers can be found (*6*).

Another way to achieve free-radical solution polymerization would be through a method of continuous-feed polymerization. In such a reaction, either the monomer or the initiator or both are fed into the polymerization system either continuously or at given intervals. A description of such a polymerization of methyl methacrylate was originally made by Riddle (*7*).

In a typical reaction of the first type, the initiator concentration changes only a few per cent during the early stages of the reaction if the reaction temperature is not too high. Such polymerizations can, therefore, be assumed to have a steady state character during this period. This fact is often taken advantage of to investigate various dependencies quantitatively. At higher temperatures, however, the square-root dependence of rates upon the initiator concentration no longer holds, because now the initiator is being depleted too rapidly.

TABLE 8-1[a]

Polymerization temp., °C	Mol. wt. in benzene	Mol. wt. in ethyl alcohol
140	53,800	51,600
170	30,500	28,900
200	21,800	23,200

[a] From Reference *5*.

In the second type of solution polymerization, where the reaction is conducted by continuously feeding the monomer or initiator or both into the reaction mixture, nonstationary state would be expected to apply. Coupek et al. (*8*) investigated such a polymerization, where the initiator was fed at a constant rate into the reaction mixture at elevated temperature. Hoffmann et al. (*9*) pointed out that in such reactions, narrow-molecular-weight distributions result for many polymers, provided the molecular weight does not exceed 100,000 and the conversions are kept below 50%.

It appears (*10*) that during such continuous-feed polymerizations, steady state conditions actually tend to predominate throughout the whole period of addition, provided the initiator is replenished at such a rate as to keep its concentration in the reaction mixture fairly constant.

The importance of the relative polarity of the solvent when solution polymerizations are carried out by ionic mechanism, was mentioned in Chapter 5. The course of these reactions is strongly affected by differences in the degree of association or dissociation of ionic species in their surrounding media.

This is true of both cationic and anionic mechanisms. A good example is work by Overberger et al. (*11*), who investigated the effect of the solvent in homogeneous anionic copolymerization of styrene with *p*-methylstyrene, *p*-tert-butylstyrene, and *m*-methylstyrene. In a nonpolar medium where lithium is the counterion, they found a heterogeneous distribution, with the more basic monomer present in higher concentrations at the growing chain end, indicating an enhanced relative reactivity. This effect, however, became depressed through the addition of small amounts of a more polar solvent. Also, in nonpolar media, an increase in temperature favored the incorporation of the less basic monomer into the chain. On the other hand, in a more polar solvent, an increase in temperature had less of an effect and favored homogeneous copolymerizations.

A similar effect of solvent polarity in styrene and *p*-methylstyrene cationic copolymerization was shown by Tobolsky and Boudreau (*12*). Here the styrene content in the copolymer decreased as the polarity of the solvent increased from toluene to nitrobenzene. The solvent polarity, however, had no effect on the copolymerization of *m*-methylstyrene with styrene. Overberger et al. (*11*) explain the observed phenomenon in cationic mechanisms on the basis of the influence of hyperconjugation. Relative reactivity is a function of the ability to stabilize the resulting carbonium ion by resonance. Increase in solvent polarity frees the carbonium ion from the counterion, and thereby permits it to interact more with the aromatic structure. This results in a decrease in styrene content in the product.

No special mention needs to be made of the role a solvent plays in condensation polymerizations. Most of these reactions, when carried out at higher temperatures, are conducted in solvent-free systems ("in the melt"). The lower-temperature interfacial polycondensations are carried out in solvents, but these are more like inert diluents, although here it appears that solvents which possess the greatest swelling power are most desired (*6*).

8-3. Suspension Polymerization

Suspension, or pearl, polymerization is a technique which is only utilized in free-radical polymerizations. The monomer is mechanically dispersed in a liquid, usually water, which is a nonsolvent for the monomer as well as for all the polymer species that form in the reaction.

Monomer-soluble initiators are preferred so that they remain dissolved in the monomer droplets throughout the course of the polymerization. For example, benzoyl peroxide is found to be five to nine times more effective in the initiation rate of polymer formation (because it is dissolved in the monomer and not in the water) then sodium persulfate or perborate, which would be dissolved in water and not in the monomer. By comparison, tertiary butyl hydroperoxide, an initiator partially soluble in monomer as well as in water, is about one-fourth as effective as benzoyl peroxide.

The organic phase in a suspension polymerization exists in water in discrete microscopic beads throughout the whole reaction, before, during, and after polymerization with a marked organic (oil) phase and an interface.

Often, no differences in rates are found for suspension and for bulk polymerization, although in some cases reaction initiations at the interface are conceivable. But, in cases like styrene, the process may be described as being essentially an effectively cooled bulk polymerization which has been broken up by dispersion in water. Kinetic data for styrene (*1*) show that initiation, propagation, and termination apparently all occur inside the pearl in the same way as in mass polymerization.

An ideal suspension polymerization utilizes monomers that are substantially insoluble in the dispersion medium, which, as already mentioned, is usually water. The dispersing of the monomer or mixture of monomers into the small globules in the nonsolvent is usually achieved by strong agitation (mechanical). A suspension stabilizer is used, the function of which is to keep globules dispersed during polymerization. As the reaction progresses, each liquid monomer globule is converted into a hard or rubbery bead (or pearl) of polymer.

The list of monomers polymerized by such a method is large. The best known are styrene, *p*-chlorostyrene, dichlorostyrene, methyl methacrylate, vinyl acetate, vinylpyridine, vinylnaphthalene, vinylcarbazol, isoprene, and cyclopentadiene. Vinyl chloride, butadiene, and isobutylene are harder to handle because of their volatility. Acrylonitrile is so water-soluble that much polymer is formed in aqueous solution. Ratios of monomer to water are most convenient when they are 1:10 or 1:8. This allows good heat transfer and makes it easy to produce and maintain separate globules. Ratios of 1:1 have, however, been used in some cases.

By adjusting the experimental conditions (such as by stirring, altering monomer-to-water ratios or the amount and nature of the suspension stabilizer, and temperature), beads whose diameters range between 0.01 and 0.5 cm can be produced without difficulty. Pearls as large as 1 cm in diameter were obtained. The smallest obtained were of 1 micron (1×10^{-3} mm) size (*13*).

Conditions for forming various bead sizes were studied by Hohenstein and Mark (*14*). Their results are summarized in Table 8-2.

A partially cross-linked pearl (insoluble in solvent, but one that can be swelled) is easily obtained by adding small percentages of a difunctional monomer to the polymerizable monomer, such as divinyl benzene, allyl methacrylate, and ethylene glycol dimethacrylate. The resulting pearls are very hard.

One method of preparing a thermosetting resin from highly cross-linked, comparatively small beads is to swell the beads with a monomer (such as styrene) containing a small amount of initiator until they become somewhat softened and increase in volume between 5 and 16%. The sticky gelatinous "dope" that is obtained can be cast, molded, or extruded in any desired form. The finished product is placed in a closed vessel and the monomer mixture is polymerized at a suitable temperature.

The addition of a small amount of a high-boiling mineral oil produces highly transparent pearls from styrene and vinyl derivatives with a high gloss. A quantity equal to 0.5% of the monomer is commonly used. The mineral oil seems to facilitate the removal of the suspension stabilizer from the beads and to decrease water absorption.

Because it is necessary to bring globules through the sticky period, the surface may be covered by either inorganic or organic substances which do not interfere with the reaction but prevent or diminish this tendency of the globules to stick together during the gummy period.

TABLE 8-2

Conditions for Forming Various Bead Sizes[a]

Monomer	Speed of agitation	Ratio of monomer to H_2O	Stabilizer	% Init.	Temp., °C	Reaction time, hours	Diameter, mm
Styrene	Medium	1:6	Talcum	1.0	90	5	1.1
	Medium	1:6	Gelatin	1.0	90	5	2.0
	Medium	1:6	Polyvinyl alcohol	1.0	90	6	3.1
	Fast	1:6	Polyvinyl alcohol	1.0	90	6	0.8
	Fast	1:4	Polyvinyl alcohol	1.0	90	5.6	0.7
Vinyl acetate	Medium	1:6	Polyvinyl alcohol	0.5	80	6	3.2
	Fast	1:6	Polyvinyl alcohol	0.5	80	6	1.4
	Fast	1:8	Polyvinyl alcohol	0.5	80	6	0.9

[a] From Reference *14*.

Among the inorganic materials that might be used are calcium salts, magnesium salts, barium carbonates, silicates, sulfates and phosphates, alumina, Fuller's earth, milk of magnesia, talc, and bentonite. Among the organic materials are gelatin, pectin, starch, algynates, methyl and hydroxyethyl celluloses, and poly(vinyl alcohol). In addition, interfacial tension between water and the monomer phase may be increased by dissolving electrolytes in the water.

8-4. Emulsion Polymerization

Vinyl monomers may also be polymerized at favorable rates by free-radical mechanism in an aqueous medium containing an emulsifier and a water-soluble initiator.

Not only is emulsion polymerization more rapid than bulk or solution polymerization when carried out at the same temperature, but, surprisingly enough, the resultant molecular weight may be much greater than that obtained at the same rate in bulk polymerization. Here the initiator radicals are generated in the aqueous phase, whereas growth and termination probably occur in the surface of the dispersed oil phase.

It has been mentioned that to date we still do not understand clearly all the aspects of the emulsion systems. But the mechanism and kinetics are now fairly clear for systems in which the monomer is water-"insoluble" and in which the polymer is soluble in the monomer. Much of the work was done by Harkins (*17*), as well as by Smith and Ewart (*18*), although their mechanism is now disputed (*15*, *16*).

Qualitative Theory

When soap is added to water in excess of a generally low critical concentration, micellar aggregates are formed (*17*). Depending on the soap and other factors, these may contain anywhere from 50 to 100 or more soap molecules, each with a diameter of about 50 A. They would be present in a concentration of some 10^{18} micellars per milliliter of water. The solubility of a monomer or other sparingly soluble organic compound is increased considerably by the presence of a soap or detergent micelle. X-ray and light-scattering measurements show that the micelles increase in size when monomer is added. This is a clear indication that the "solubilized" monomer molecules occur in the micelles, presumably among the hydrocarbon chains, that occupy the interior.

The proportion of monomer initially present in an emulsion polymerization mixture is much greater than can be accommodated by the soap micelles. This means that most of the monomer occurs as droplets much larger in size than the micelles, a micron or more in diameter (10,000 A), depending on agitation, which may be stabilized by a portion of the soap. This would mean that there are roughly 1×10^{11} droplets per milliliter of water in the commonly used ratios of the monomer-to-water phase.

The picture thus emerges that while most of the monomer is initially present in macroscopic droplets, most of the soap occurs in the micelles. More important, the micelles present a much greater total surface than the droplets, although the total volume of micelles is considerably less than the droplets.

Schematically we might represent the process of swelling the soap micelles by monomer as shown in Figure 8-1. Because these micelles are highly swollen by water, they permit free diffusion of the water-soluble initiator.

If the initiator, hydrogen peroxide, or ammonium persulfate is now added to the emulsion it will decompose (provided the temperatures are great enough) into radicals or radical ions. The reaction is further enhanced by the presence of reducing or oxidizing ions, which cause such decomposition through an electron-transfer reaction. In the case of potassium persulfate, at 50°C, some 10^{13} radicals ($SO_4^-\cdot$) are formed per milliliter of water per second, again at the commonly used concentration of the initiator. Such radical ions then react with small amounts of monomer dissolved in the aqueous phase, forming organic sulfate radical ions. After the reaction with these few monomer ions has taken place, the product, also a radical ion, now contains an organic molecule as part of its makeup. The product can now become incorporated into a micelle, because of the dynamic character of the equilibrium between the micellar and molecularly dissolved emulsifier. According to Harkins (*17*) and Smith and Ewart (*18*), in the interior of the micelle, the organic portion of the entered radical encounters a high concentration of solubilized monomer and, therefore, chain growth proceeds rapidly.

Once the polymerization was initiated, the system is in a state of changing equilibrium. Additional monomer diffuses rapidly from the relatively large monomer droplets or even from other micelles (in the attempt of the system to maintain its equilibrium) into the active micelle. The active micelle then swells because of the presence of polymer chains. For example, in the polymerization of styrene at 50°C, a micelle, after being "stung" by a radical, expands in 1 minute to about 250 times its original volume. The growth of a "stung" micelle is accompanied by formation of a new polymer-water interface onto which soap or emulsifier molecules are absorbed from the aqueous phase. As a result, the equilibrium condition between the molecularly dissolved soap and micellar

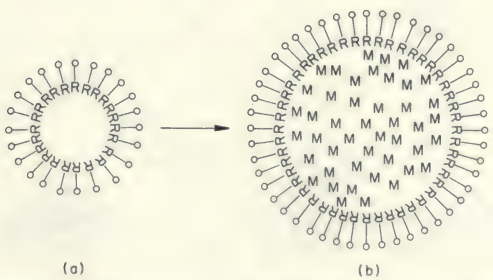


Figure 8-1. (a) Original soap micelle; (b) micelle swollen by monomer.

soap becomes disturbed, and micelles disintegrate to restore the concentration of molecularly dissolved emulsifier to its equilibrium value. In this process of the formation of each polymer particle many micelles will disappear. However, only a small fraction of the original micelles are transformed into polymer particles, and the final latex contains some 10^{15} particles per milliliter of water. This process of particle formation results in absorption of the emulsifier onto polymer particles early in the reaction. Finally, after about 10–20% conversion, no micelles exist and so no new particles are formed. Polymerization inside a micelle or polymer particle does not at this stage deplete the particle of monomer. This is caused by osmotic forces which cause the amount of monomer diffusing from the droplets through the water to the particles to be maintained in excess of the amount consumed by polymerization.

Provided the monomer droplets are sufficiently small, which is usually the case with adequate agitation, diffusion will be rapid enough to replace the monomer consumed in the reaction and to supply the additional amount required for equilibrium swelling of polymer particles. Owing to this swelling, monomer droplets will disappear from the reaction mixture before polymerization is completed. From this moment on, the reaction will slow down. Final high conversion is usually possible. Actually, the equilibrium process can be repeated many times, until all the monomer is used up. Schematically this can be represented as shown in Figure 8-2.

In an emulsion system, therefore, a growing molecule is visualized as subject to restrictions favoring growth and not termination, because (*17*, *18*):

1. The polymer is formed in a coiled state or at least not fully extended.
2. It exists in a swollen state of high viscosity.
3. Internal conditions are set up by the existence of soap.
4. Monomer supply is high, owing to the process of diffusion to the polymer.

Although it is possible to carry out thermal polymerization in an emulsion, it is much more convenient to employ additional sources of free radicals to

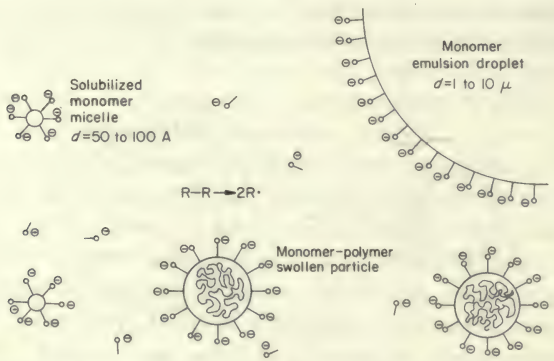


Figure 8-2. Early stages of emulsion polymerization.

start chain growth. Gamma-rays and photolysis of photosensitive compounds may be used occasionally. In most cases, however, radicals are formed chemically. Persulfates are good examples of such initiators, yielding anionic radical ions upon decomposition. The anionic character of these radicals will prevent or at least impede their diffusion into negatively charged micelles or particles present when anionic emulsifiers are used. But because these radical ions are efficient initiators in emulsion polymerizations, it is likely that initiations occur in the aqueous phase even in the case of water-"insoluble" monomer. So it must be assumed that by very slow polymerization, oligomeric radicals are formed carrying a sulfate group. The presence of sulfate groups on polystyrene produced at 50°C with a persulfate catalyst was demonstrated by the use of a dye-partition method adopted from a procedure with surfactants developed by Jones (*19*) and Van der Hoft (*20*). After correction for transfer to the monomer, at least 70% of the remaining polymer molecule ends were found to carry sulfate groups.

It is believed that the rate of decomposition of peroxide compounds is actually greater in emulsion than in solution. Evidence has been presented that the decomposition rate of cumene hydroperoxide, for example, in a polymerizing emulsion system is several magnitudes of that in a styrene solution (*21*). This suggests that the enhanced decomposition rate is an interfacial phenomenon. It is conceivable that in the case of a hydroperoxide, the two radicals are formed in such a way that only the organic radical (RO·) enters the organic phase, while the inorganic fragment (HO·) remains in the aqueous phase, where it can undergo further reactions. This means that radicals enter the organic phase one by one, as in the case of water-soluble initiators.

In a normal emulsion system the energy of activation of initiation was found to be about 17,000 calories per mole. In an emulsion system using redox initiation, however, the energy is about 10,000 calories per mole, showing that this is a very efficient way to produce radicals at low temperatures.

Bacon (*21*) presented rate curves for polymerizations of acryllonitrile in an aqueous solution and in an emulsion as well as in an emulsion with a redox system. This demonstrates quite effectively the advantages of redox initiation. They are reproduced in Figure 8-3.

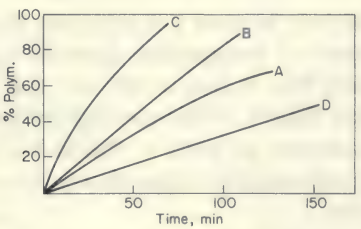


Figure 8-3. Approximate rate curves for polymerization of acrylonitrile: A, redox system at 30°C; B, redox system at 40°C; C, redox system at 50°C; D, no reducing ion.

When persulfates are employed in a redox system, the reactions can be written as follows:

$$S_2O_8^{2-} + \text{red. agent} \rightarrow SO_4^{2-} + SO_4^{-}\cdot + \text{red}^{+}$$

$$SO_4^{-}\cdot + H_2O \rightarrow HO\cdot + SO_4^{2-}$$

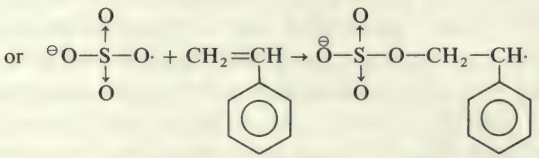
when the reducing agent is $S_2O_3^{2-}$,

$$S_2O_8^{2-} + S_2O_3^{2-} \rightarrow SO_4^{2-} + SO_4^{-}\cdot + S_2O_3^{-}$$

Initiation:

$$SO_4^{-}\cdot + \text{monomer} \rightarrow \text{adduct}$$

or



In the case of hydrogen peroxide and a ferrous ion, the reaction is actually quite similar:

$$H_2O_2 + Fe^{2+} \rightarrow HO\cdot + Fe^{3+} + OH$$

$$Fe^{2+} + HO\cdot \rightarrow Fe^{3+} + OH^{\ominus}$$

$$H_2O_2 + HO\cdot \rightarrow H_2O + HOO\cdot$$

$$Fe^{2+} + HOO\cdot \rightarrow Fe^{3+} + HOO^{\ominus}$$

$$Fe^{3+} + HOO\cdot \rightarrow Fe^{2+} + O_2 + H^{\oplus}$$

The hydroxyl radical is a very reactive radical toward olefinic monomers.

In addition to the four ingredients (peroxide, monomer, soap, and water) there is often usually a fifth ingredient present, one that is sometimes called a "modifier." These so-called modifiers are actually effective chain-transferring agents used to regulate molecular weights (Chapter 4):

1. $\sim\!\sim M\cdot + HSR \rightarrow \sim\!\sim MH + RS\cdot$

2. $RS\cdot + M \xrightarrow{\text{fast}} RSM\cdot$

Step 2 does not affect the rate, because it is relatively fast.

The choice of structures of mercaptans depends upon the nature of the individual polymerization. This is due to the fact that in the emulsion polymerization, the molecular weight of the mercaptans will regulate the rate of their migration from monomer droplets to the loci of polymerization. High-molecular-weight mercaptans migrate more slowly. In solution polymerization such problems do not arise.

The above emulsion-polymerization mechanism was that of Harkins (*17*) and Smith and Ewart (*18*). Brodnyan and co-workers (*15*, *16*) introduced strong doubt about the complete adequacy of such a mechanism and actually offered

evidence that the propagation might be taking place on the surface of the polymer particle.

Specifically, if the Harkins (*17*) and Smith and Ewart (*18*) picture is correct, propagation takes place inside the monomer–polymer particle, and after the monomer droplets disappear, at about 50–70% conversion, the reaction proceeds exactly like bulk polymerization. In such a picture more branching should be expected between 0 and 50% conversion than in the bulk systems. On the other hand, if the reaction occurs at the surface, then most of the polymer in the monomer–polymer particle will be inside the center of the particle and the monomer at the surface, where the reaction is taking place. In such a situation we should expect that much less chain transferring to polymer molecules occurs, with the resultant low degree of branching, until the conversion of 80–90% is reached. This means that if the second picture is correct, polymers prepared by emulsion polymerization should be less branched than those produced in bulk. The results of Brodnyan et al. (*16*) indicated that fewer branched polymers actually result from emulsion polymerizations than from bulk.

8-5. Inverse Emulsion Polymerization

In an inverse emulsion polymerization (*22*), a hydrophilic monomer, frequently in aqueous solution, is emulsified in a continuous oil phase, using water in an oil emulsifier; it is then polymerized using an oil-soluble initiator. The products are viscous lattices comprised of submicroscopic, water-swollen, hydrophilic polymer particles colloidally suspended in the continuous oil phase. The average size of these lattices is as small as 0.05 micron. The technique is applicable to a wide variety of hydrophilic monomers and oil media. Inverse emulsion polymerization, shown in Figure 8-4 is the opposite of regular emulsion polymerization.

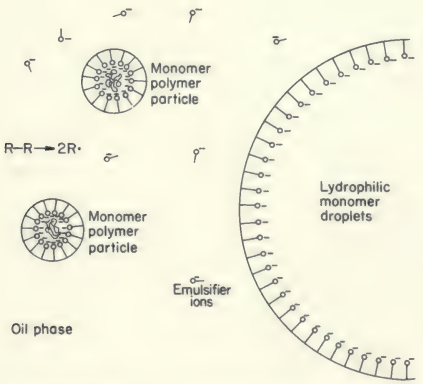


Figure 8-4. Inverse emulsion polymerization. (From Reference *22*.)

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Part III

COMMON ADDITION POLYMERS

Macroalkanes

9

9-1. Polymers from Azoalkanes

Perhaps the simplest macromolecular alkane is polymethylene. Essentially such a polymer, or one that to all intents and purposes is the same thing, is now made industrially through polymerization of ethylene. However, the first reported synthesis of a straight-chain macroparaffin was accomplished by von Pechmann (*1*), who obtained small amounts of a white flocculant powder which separated from an ether solution of diazomethane. This material was demonstrated by Bamberger and Tschirner (*2*) to actually be polymethylene, $+CH_2+$, which melted at 128°C.

During recent years, the synthesis of polymethylene from diazomethane was much improved by employing various catalysts. Buckley and co-workers (*3*) demonstrated that the material is a straight-chain hydrocarbon, highly crystalline, with a melting point as high as 136.5°C possible. Renfrew and Morgan (*4*) offered some proof that the molecular weight might be in the millions.

Since the days of Bamberger and Tschirner, many catalytic systems were found for azomethane polymerization. Thus Meerwein (*5*) demonstrated that the reaction is catalyzed by a wide variety of boron compounds (such as halides, alkoxides, and alkyls). Others have demonstrated that gold is also a useful catalyst. Several different mechanisms may actually be involved in these polymerizations, depending upon the nature of the catalyst. Bawn et al. (*6*) suggest that the mechanism of polymerization that takes place when boron fluoride catalysis is employed involves the formation of a carbonium ion intermediate,

$$BF_3 + CH_2N_2 \rightarrow F_3\overset{\ominus}{B}-CH_2-\overset{\oplus}{N}\equiv N \rightarrow F_3\overset{\ominus}{B}-\overset{\oplus}{C}H_2 + N_2$$

$$F_3\overset{\ominus}{B}-\overset{\oplus}{C}H_2 \rightarrow F_2B-CH_2F \xrightarrow{CH_2N_2} F_2\overset{\ominus}{B}(CH_2F)-CH_2-\overset{\oplus}{N}\equiv N \rightarrow F_2\overset{\ominus}{B}(CH_2F)-\overset{\oplus}{C}H_2 + N_2 \rightarrow F_2B(CH_2)_2F$$

Long hydrocarbon chains are synthesized in this manner, and the formed polymer possesses the structure $F_2B(CH_2)_nF$. The resulting molecule is still active toward more diazoalkanes; if one introduces these polymers after purification into a solution of a different diazocompound, block copolymers can result,

$$F_2B(CH_2)_n\underset{\displaystyle R}{(CH)_m}F$$

When copper powder or colloidal gold are used as catalysts instead, a carbene intermediate was postulated (*7–9*). Gold is particularly useful in forming an isotatic polyethylidine, but in low yields (*10, 11*). Nasini and Trossarelli (*12*) investigated the chemical structure of polyethylidine obtained from diazoethane. They noted that the amount of crystallinity in polymer obtained by gold catalysis is 65%, and that of the amorphous polymer 35%. In addition, in the course of the reaction, low-molecular by-products form, such as *cis*-butene-2 and *trans*-butene-2 in nearly equal amounts. The polymer itself (either the amorphous or the crystalline) possesses terminal unsaturation (*13, 14*). So they propose the following mechanism of reaction:

The first step, adsorption through the lone electron pair of a diazoethane molecule on the gold surface takes place:

$$\begin{array}{l} \qquad\qquad\quad CH_3 \\ \qquad\qquad\quad | \\ H-\overset{\ominus}{\underset{\cdot\cdot}{C}}-\overset{\oplus}{N}\equiv N \\ Au\quad Au\quad Au\quad Au\quad Au\quad Au\quad Au\quad Au \end{array}$$

The polarization of the carbon-gold bond causes rupture of the nitrogen carbon bond of the diazoalkane, releasing nitrogen and binding the highly unstable ethylidine fragments on the metal surface. Part of the ethylidine fragments can then be desorbed from the metal surface and rearranged to ethylene or react with a diazoethane molecule, thereby yielding an adsorption product that can either be given off as butene-2 or can initiate a polyalkylidine chain as follows:

$$\begin{array}{l} \qquad\quad CH_3 \qquad\qquad\qquad\qquad\qquad\qquad\quad CH_3 \\ \qquad\quad | \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ \qquad\quad CH_2 + CH_3CH-N_2 \rightarrow H\ \ CH_2=CH-CH + N_2 \\ Au\quad Au\quad Au\quad Au\quad Au\quad Au\quad Au\quad Au \end{array}$$

leading to the formation of a terminal vinyl group.

The amorphous polymer, they postulate, would be formed through the insertion of diazoethane from solution at the end of the chain attached to the metal surface:

$$\begin{array}{l} \qquad\qquad\quad CH_3 \qquad\qquad\qquad\qquad\qquad\qquad\quad CH_3\ \ CH_3 \\ \qquad\qquad\quad | \qquad\qquad\qquad\qquad\qquad\qquad\quad | \qquad | \\ H\ \ CH_2=CH-CH + CH_3-CH-N_2 \rightarrow H\ \ CH_2=CH-CH-CH + N_2 \\ Au\quad Au\quad Au\quad Au\quad Au\quad Au\qquad\qquad Au\quad Au\quad Au\quad Au\quad Au \end{array}$$

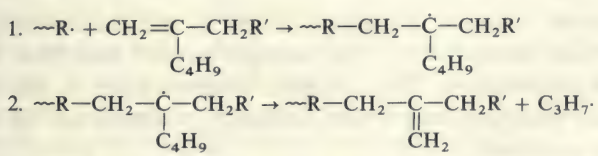
9-2. Polyalkanes from Carbon Monoxide

An interesting, but different, means of macroparaffin synthesis comes through hydrogenating carbon monoxide, usually under pressure and in the presence of some transition-metal catalysts, such as finely divided ruthenium. This process, originally reported by Pichler (*15*) was further investigated by Kolbel and co-workers (*16*), who obtained relatively low molecular weight paraffins (up to 7000) with finely divided metallic ruthenium in water at pressures of 75–200 atmospheres and temperatures of 150–260°C. Recently, Pichler and co-workers (*17*) carried this reaction out at high pressure but at temperatures below 140°C and obtained polymethylene of molecular weights higher than 100,000.

9-3. Polyethylene

The conversion of olefinic molecules, specifically ethylene by a free-radical mechanism to macroparaffins, was first reported by Fawcett and co-workers (*18*). They found that the reaction conditions required at least 500 atmospheres pressure. The molecular weight of the product showed an increase with the increase in the pressure of the reaction, the maximum being reached at 3000 atmospheres. In this reaction, the degree of branching decreased with the increase in the pressure, the product, being essentially linear when 5000 atmospheres were used. Lower pressures are generally employed, however, to produce a branched (low-density) material.

Ehrlich et al. (*19, 20*) investigated this reaction, which they initiated by di-*t*-butyl peroxide, using 750–3000 atmospheres pressure and 130–250°C. He found that the methyl and vinylidine contents per each 1000 CH_2 groups in the product decreased with an increase in pressure and increased with the increase in temperature. The vinylidine content appears to be more strongly affected by these parameters than the methyl content. The unsaturation in most products is apparently in the form of the vinylidine structure, but the vinyl structure becomes competitive at high temperatures and high pressures. There also appears to be a close correspondence between the vinylidine content and molecular weight. The β-elimination in the decomposition of a tertiary polymer radical could lead to this result. This was suggested by Oaks and Richards (*21*) and is presented by Woodbrey and Ehrlich (*20*) as follows:



where R represents a long chain and R′ a short chain branch. This reaction was thought (*21*) to take place above 290°C. It could conceivably also take place in high-pressure polymerizations of ethylene, according to Nicolas (*22*).

Tertiary carbons can be the products of two consecutive intramolecular hydrogen abstractions ("backbiting") (*23*). By using as an example a 1,5 transfer

$$RC_4H_8\dot{C}H_2 \rightarrow R\dot{C}HC_4H_9$$

followed by two addition steps and then a second abstraction step, one obtains the tertiary carbon

$$RCH(C_4H_9)C_3H_6\dot{C}H_2 \rightarrow R\dot{C}(C_4H_9)_2$$

The above mechanism does not explain the origin of the ethyl branches. And it was shown that commercial high-pressure polyethylene possesses as many ethyl groups as butyl groups and possibly even twice as many (*24*, *25*). One mechanism was originally proposed to explain this, based on the idea of isomerization of an unbranched radical. Some evidence, however, was presented (*20*) to show that this mechanism may not be quite correct.

The fact that ethylene polymerizes at high temperature and high pressure is rather interesting, because Waterman and Tulleners (*26*) demonstrated that this molecule actually tends to decompose under these conditions into carbon, hydrogen, and methane. The polymerization reaction itself is exothermic, and proper control of the temperature is required to avoid explosions.

Although the behavior of ethylene in free-radical polymerization is sufficiently similar to typical vinyl-type free-radical polymerizations to be able to follow the general scheme, high-molecular-weight polymers will not form when the reaction is carried out at low pressure. This was demonstrated by Danby and Hinselwood (*27*) to be due to a great tendency for the radical chains to undergo changes during the reaction, which results in chain termination. This might perhaps be explained by the fact that maximum density of compressed ethylene is only 28 g per mm^3 at pressures below 300 atmospheres and 150°C. Yet, for the propagation to proceed to a high molecular weight, greater closeness of ethylene molecules to each other appears necessary.

In high-pressure polymerizations oxygen can act as an initiator. Other initiators are various peroxides and hydroperoxides and azo compounds. Impurities, such as acetylene or hydrogen, act as chain-transferring agents and must be carefully removed.

When 2000 atmospheres pressure is reached at 165°C, the maximum safe oxygen content of ethylene gas is 0.075%. Any oxygen beyond that limit will cause an explosive decomposition. The oxygen concentration is directly proportional to the per cent conversion and inversely proportional to the molecular weight of the polymer.

A typical industrial reaction for the preparation of low-density polyethylene is one usually carried out in a tubular reactor or a high-pressure tower with the unreacted ethylene recycled.

Benzene or chlorobenzene are often used as the reaction solvent in which both the monomer and polymer are soluble at elevated temperatures. Some techniques call for addition of water, which tends to dissipate the heat. About 1500 atmospheres of pressure at 190–200°C is considered the preferred condition with 0.03–0.10% oxygen present,

$$n\mathrm{CH_2{=}CH_2} \xrightarrow[\substack{0.03\text{–}0.10\,\%\,\mathrm{O_2}\\ 1500\ \mathrm{atm}}]{190\text{–}210^\circ\mathrm{C}} +\mathrm{CH_2{-}CH_2}+_n$$

As stated, it was demonstrated (*23*, *28*, *29*) that low-density polyethylene is branched. Actually there are two types of branches, one of them arising from chain transferring to the polymer. This type of branching usually results in long branches which may equal in length the main chain. The other type are the short branches, perhaps not longer than four carbons in length. A typical low-density polyethylene molecule might possess only one long branch and perhaps as many as forty or fifty of the short ones. Kokle and co-workers (*30*) reported that the molecular-weight distribution of such material is very broad, $\overline{M}_w/\overline{M}_n = 20\text{–}50$.

Although high-density, linear polyethylene can be synthesized by this free-radical mechanism using very high pressures, industrially much of it is produced either with the aid of Ziegler catalysis or by using metal-oxide-support catalysts (Chapter 6). Among the many catalyst systems that sprang from the original work by Ziegler, those using aluminum alkyls and titanium chlorides are the main ones employed throughout much of industry. Saturated aliphatic hydrocarbons serve as solvents and dispersants for both colloidal dispersion of the catalyst and the polymeric products. Slight pressures are usually used to introduce the ethylene at temperatures of 50–75°C. The reaction is exothermic and requires cooling. Upon completion of the reaction, the catalyst is quenched with water or alcohol.

When metal-oxide-support catalysts are employed (which can be used as either fixed or fluid beds), higher pressures, up to 500 psi must be used at temperatures of 60–200°C.

Typical linear polyethylene is highly crystalline, the crystallinity sometimes exceeding 90%. The polymer contains less than one side chain per every 200 carbons on the backbone. The density of this material ranges from 0.95 to 0.97, whereas, low-density polyethylene ranges from 0.92 to 0.93.

The melting point of commercial low-density polyethylene is approximately 108–111°C and high-density polyethylene between 124 and 134°C. The tensile strength of low-density polyethylene ranges from 1800 to 2000 psi and that of high density polyethylene from 3500 to 4500 psi.

Polyethylene is soluble in aromatic and chlorinated solvents at elevated temperatures. Although it is inert to acids and alkalies, it will oxidize when attacked by strong oxidizing acids.

9-4. Polypropylene

Polypropylene cannot be prepared in high molecular weights by free-radical polymerizations. Mortimer and Arnold (*31*) investigated free-radical polymerization of propylene and other α-olefins. They concluded that these polymerizations appear to be completely controlled by chain transferring.

High-molecular-weight polypropylene of varying degrees of crystallinity and stereospecificity can, however, be readily prepared with coordination catalysts using techniques developed by Natta and co-workers (*32*) (Chapter 6). A summary of the catalytic systems and the amount of crystallinity as found by Natta et al. (*33*) is shown in Table 9-1. Natta and co-workers (*32*) also concluded that the kinetics of reactions which result in both atactic and isotactic polypropylene are essentially the same.

In addition, Natta and co-workers found (*34*) that monoalkylaluminum dihalides when used in combination with titanium trichloride and some Lewis bases yield highly stereospecific polypropylene at 70°C. This is shown in Table 9-2. Although isotactic poly-α-olefins are more common, preparation of syndiotactic polypropylene was also reported (*35*).

Yugachi and Iwamoto (*36*) also reported that they achieved a 1,3 type of polymerization of propylene with VCl_4 + Fe(acetylacetone)$_3$ adduct (in a 1:1 ratio) and $(C_2H_5)_3Al$, using benzene, 1,2-dichloroethane, or chlorobenzene as

TABLE 9-1

Coordination Catalysts for Polymerization of Propylene[a]

Metal halide	Metal alkyl	Crystallinity in polymer, %
$TiCl_3$(α, γ, or δ)	$Al(C_2H_5)_3$	96–98
	$Al(C_2H_5)_2Cl$	96–98
	$Be(C_2H_5)_2$	94–96
	$Mg(C_2H_5)_2$	78–85
	$Zn(C_2H_5)_2$	30–40
	NaR	0
$TiCl_3$(β)	$Al(C_2H_5)_3$	40–50
T_1Cl_4	$Al(C_2H_5)_3$	48
	$Al(C_3H_7)_3$	51
	$Al(n\text{-}C_4H_9)_3$	30
	$Al(i\text{-}C_4H_9)_3$	60
$TiBr_4$	$Al(C_2H_5)_3$	80–92
VCl_3	$Al(C_2H_5)_3$	73
VCl_4	$Al(C_2H_5)_3$	48
$VOCl_3$	$Al(C_2H_5)_3$	32
$ZnCl_2$	$Al(C_2H_5)_3$	55
$CrCl_3$	$Al(C_2H_5)_3$	36

[a] From Reference *33*.

TABLE 9-2
Influence of Lewis Bases on Stereospecific Polymerization of Polypropylene[a]

	Crystalline material, %
Pyridine + $2Al(C_2H_5)Br_2$	>98.5
$N(C_2H_5)_3 + 2Al(C_2H_5)Cl_2$	95
$NH(C_2H_5)_2 + 2Al(C_2H_5)Cl_2$	93
$\overset{\oplus}{N}(C_4H_9)_4I^{\ominus} + 2Al(C_2H_5)Br_2$	>99
$\overset{\oplus}{N}(C_4H_9)_4Br^{\ominus} + 2Al(C_2H_5)Cl_2$	96

[a] From Reference *34*.

solvents. Such a reaction is effectively a hydride-shift type of polymerization. Actually their product was a copolymer of the 1,3 and 1,2 adducts:

$$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{CH}} \rightarrow \text{+}CH_2{-}CH_2{-}CH_2\text{+}_x\text{+}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{+}_y$$

The crystalline structure of this product was found to be similar to that of ethylene propylene copolymer.

9-5. Higher Poly-α-olefins

By now, many α-olefins have been polymerized into crystalline polymers. Campbell and Haven (*37*) have summarized the melting points of a number of these polyolefins, as shown in Table 9-3.

The data shown in this table are quite significant because a number of stereospecific polyolefins with long, pendant R groups in the structure

$$\text{+}CH_2{-}CHR\text{+}_n$$

exhibit such high melting points. This is explained on the basis of geometric shapes of the polymeric molecules in the crystallites.

Dunham and co-workers (*38*), using $VCl_3{-}Al(C_2H_5)_3$ as the catalyst, reported polymerizations of a number of α-olefins of the general structure

$$CH_2{=}\underset{\displaystyle (CH_2)_x}{\underset{|}{CH}}$$
$$\underset{\displaystyle R}{|}$$

where R = CH_3; $CH(CH_3)_2$; $C(CH_3)_3$; C_6H_5, and x = 0–3. The reactions were carried out without the aid of a solvent. The products showed less stereoregularity than was obtained with other catalysts by Natta et al. (*39*) using titanium halides. Higher conversions, however, were found to be possible.

Coover and Joyner (*40*) investigated the effects of additions of Lewis bases to aluminum–alkyl dihalide and transition-metal halide catalysts on

TABLE 9-3

Melting Points of Polyolefins[a]

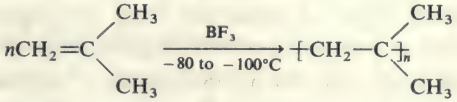
Monomer	m.p., °C	State
$CH_2=CH_2$	136	Crystalline
$CH_3CH=CH_2$	165	Crystalline
$CH_3CH_2CH=CH_2$	125	Crystalline
$CH_3(CH_2)_2CH=CH_2$	75	Crystalline
$CH_3(CH_2)_3CH=CH_2$	(−50)	Rubber, noncrystalline
$CH_3(CH_2)_9CH=CH_2$	45	
$CH_3(CH_2)_{15}CH=CH_2$	70;100	Crystallinity in lateral groups
$CH_3-\underset{\displaystyle CH_3}{\overset{}{CH}}CH=CH_2$	280–285	Hard, crystalline
$CH_3-\underset{\displaystyle CH_3}{\overset{}{CH}}-CH_2-CH=CH_2$	200–240	Highly crystalline
$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-CH_2-CH=CH_2$	320	Hard, crystalline
$CH_3-CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-CH_2-CH=CH_2$	350	Hard, crystalline
$CH_3-CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-CH_2-CH=CH_2$	160	Hard, crystalline
$CH_3-\underset{\displaystyle CH_3}{\overset{}{CH}}-CH_2CH_2CH=CH_2$	110;130	Rubber, amorphous
$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-CH_2CH_2CH=CH_2$	—	—
$-CH_2CH_2CH=CH_2$	158	Slightly rubbery, but crystalline
$CH_3-CH-CH=CH_2$	360	Intractable, but crystalline
$-CH_2-CH_2-CH_2-CH=CH_2$	—	Rubber, amorphous
$-CH=CH_2$	240	Brittle, crystalline
CH_3 $-CH=CH_2$	—	Amorphous

[a] From Reference *37*.

stereospecificity of the products in α-olefin polymerizations. The bases studied were $(C_4H_9)_2O$, $(C_4H_9)_3N$, and $(C_4H_9)_3P$. It was found that stereospecificity here tended to increase with increase in basicity of the Lewis bases.

9-6. Cationic Polymerization of Olefins

Isobutene polymerizes readily by cationic mechanism. This reaction proceeds at low temperatures. The mechanism of such a reaction was discussed in Chapter 5. To achieve high molecular weights, low temperatures and low-boiling diluents are used. The reaction is exothermic and rapid. It is sensitive to the proper choice of the catalyst and also to impurities. A typical reaction is often carried out in a low-boiling alkane, or an alkyl halide or carbon disulfide, at $-80°C$ with BF_3 as the catalyst,

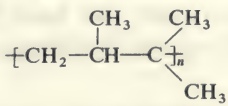


The monomer-to-diluent ratio can be approximately 1:3.

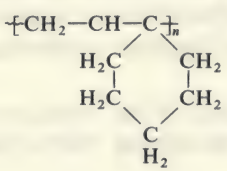
Butyl rubber is a copolymer of isobutylene with isoprene, which is needed for vulcanization (*41*). In these copolymers the diene in the monomer mixture comprises only 2–3%, or even less. These polymerizations are usually carried out in methyl chloride with $AlCl_3$ as the catalyst.

The polymer is amorphous but will crystallize when fully stretched. A study of the crystal structure suggests a helix with a head-to-tail arrangement. The isoprene is present as a 1,4 adduct. When butyl rubber is unvulcanized it has the density of 0.92.

3,3-Dimethyl-1-butene will also undergo cationic polymerization, but an isomerization accompanies the reaction (*42–44*). The reaction can be carried out with $AlCl_3$ in ethyl chloride (*42*) at temperatures between -31 and $-130°C$ to obtain mostly a liquid trimer. When a $-130°C$ reaction temperature is used, however, a solid polymer results. The amorphous product melts between 55 and 66°C and the DP is $\simeq 68$. NMR and infrared data suggest that the structure is predominantly



A hydride-shift isomerization polymerization will also occur with vinyl cyclohexane when this cationic reaction is carried out with $AlCl_3$ catalyst at temperature ranges from -144 to $+7°C$ (*44*). NMR data have shown that the product is predominantly



9-7. Copolymers of Olefins

Copolymerization of ethylene and propylene can lead to amorphous structures that can be useful as synthetic rubbers. Natta et al. (*45*), who investigated copolymerization with the aid of coordination catalysis, reported that the properties of these copolymers are determined not only by the overall ethylene-to-propylene ratios but also by the distribution of the two monomers over the polymer molecules and by their arrangement within the molecule. He concluded that the most desirable rubber-like properties are obtained when the two monomers alternate in the molecule.

Van Schooten and co-workers (*46*) investigated the structure of ethylene–propylene copolymers prepared with $VOCl_3$ or $VO(OR)_3$ catalysts and found that they have methylene sequences of two and four units. Infrared data indicate that these copolymers differ in structure from hydrogenated polyisoprene, which can be regarded as a perfectly alternating ethylene–propylene copolymer.

Bushnick (*47*) reported the copolymerization of ethylene and propylene with diisobutyl aluminum chloride and various vanadium compounds. He found that the reactivity values decreased in the order $VO(O\text{-}_nC_4H_9)_3 > VOCl(OC_2H_5)_2 > VOCl_2OC_2H_5 > VO(OC_2H_5)_3 \simeq VOCl_3$. All catalyst systems appeared very sensitive to changes in the concentration of ethylene in the mixture of monomers. All catalysts, with exception of $VOCl_3$, appeared to yield random copolymers.

Kelly and co-workers (*48*) found that homogenous catalyst systems based on alkyl aluminum halides combined with vanadium oxytrichloride or tetrachloride produced highly random ethylene-propylene copolymers with high catalyst efficiency.

We have no information yet about the manner in which propylene is placed into these alternating random copolymers prepared with vanadium-containing catalysts, that is, whether all placements are uniformly head to tail or not.

Natta and co-workers (*49*) also synthesized numerous alternating copolymers of ethylene with olefins containing an internal double bond in the *cis* configuration. These copolymers were crystalline and included butene-2, cyclopentene, and cycloheptene. Such copolymers can have four different structures: (1) threodiisotactic, (2) erythrodiisotactic, (3) threodisyndiotactic, or (4) erythrodisyndiotactic.

Corradini and Ganis (*50*) examined the structure of ethylene-*cis*-butene-2 copolymer prepared by Natta et al. (*49*) by means of X rays. They found the configuration to be erythrodiisotactic. Successive structural units were found to be repeating along the chain through the operation of a center of symmetry.

The above results agree well with the conclusions drawn about the structure of the crystalline ethylene-cyclopentene copolymer (*51*), which also was found to be erythrodiisotactic.

Although the above pertained to the formation of ethylene copolymers with other olefins by means of the Ziegler–Natta catalysis, copolymerization to

low-molecular-weight liquids over supported-metal-oxide catalysts has been known for some time now. Recently, however, solid polymers were formed as well (*52*). The structure of the products indicates some pendant alkyl groups, and in the case of ethylene-propylene copolymer an increase was observed in unsaturation from 1 % of vinylene for ethylene homopolymer to 25 % of vinylene for the copolymer. This suggests that every fourth molecule of this copolymer was evidently terminated by a propylene monomer. Such a copolymer was shown to contain 44 methyl branches per 1000 carbon atoms, indicating one propylene unit per every 10 ethylene molecules.

Copolymerization with butene over these metal oxide catalysts also leads to an increase in vinylene unsaturation (*53*).

9-8. Copolymers with Polar Monomers

High-molecular-weight copolymers of ethylene can be formed by free-radical mechanism. A wide range of compositions is possible when high pressures are used. These syntheses follow normal free-radical copolymerization kinetics. Thompson and Raines (*54*) investigated the copolymerization of ethylene with *n*-butyl acrylate, vinyl acetate, vinyl chloride, and vinyl fluoride. They found that the copolymers were random. They also found that for ethylene vinyl acetate copolymerization r_1 essentially equaled r_2, both being close to 1.

Many other radical-initiated copolymers were also prepared using emulsion systems at relatively low pressures. Thus copolymers were formed with diethylfumarate, vinyl chloride, ethyl acrylate, and maleic anhydride, the latter forming a 1 : 1 type copolymer (*55*, *56*). Vinyl acetate copolymers with ethylene are easily prepared in an emulsion-type polymerization by free-radical mechanism. These copolymers are now produced in large commercial quantities in varying ratios of vinyl acetate to ethylene.

Ethylene will also copolymerize with carbon monoxide to form a polyketone (*57*, *58*). The reaction takes place in bulk via a free-radical mechanism,

$$CH_2{=}CH_2 + CO \xrightarrow[135°C,\ 4500\text{–}14{,}700\ lb]{t\text{-butylperoxide}} \left[(CH_2{-}CH_2)_x{-}\overset{\overset{O}{\|}}{C}\right]_n$$

The reactivity ratios favor a 1 : 1 copolymer, but lesser amounts of carbon monoxide may be used, depending upon the nature of copolymer sought.

A very similar 1 : 1 copolymerization of α-olefins with sulfur dioxide is also possible (*59–62*). The reaction can actually be carried out at room temperature or lower, depending upon the structure of the olefin,

$$RCR'{=}CH_2 + SO_2 \rightarrow \left[\begin{array}{c} R' \\ | \\ C \\ | \\ R \end{array}{-}CH_2{-}\begin{array}{c} O \\ \| \\ S \\ | \\ O \end{array}\right]_m$$

where $R=R'=H$; CH_3; or $R'=H$; $R=CH_3$; $CH_3(CH_2)_n$; C_6H_5; $(CH_2)_8CO_2H$, and $n=|O$.

The structure of the adducts was shown to be head to tail (*63*). The best copolymerization temperatures depend upon the structure of the olefin. The mechanism of copolymerization has been described (*64*, *65*). It involves addition of monomer to the free-radical chain end.

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10

Polymers and Copolymers from Dienes and Polyenes

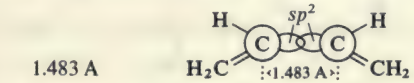
The conjugated dienes can be polymerized by free-radical, ionic, and coordination mechanisms. The composition of the products from these reactions often depends upon the polymerization methods used.

10-1. Polymers from Butadiene

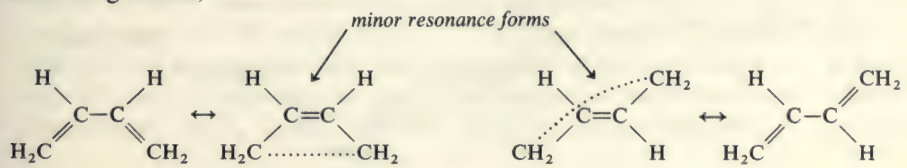
Butadiene monomer, the simplest member of the conjugated dienes, can be synthesized by dehydrogenation of butene-1:

$$\underset{}{CH_3-CH_2-CH=CH_2} \xrightarrow[cat]{\Delta} \underset{1}{CH_2}=\underset{2}{CH}-\underset{3}{CH}=\underset{4}{CH_2}$$

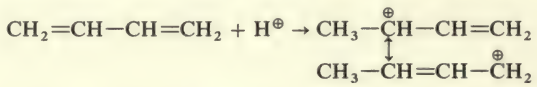
The C_2-C_3 single bond in this molecule is only 1.483 A in length and shorter than the regular C—C single bond. This was ascribed in the past to conjugation. Today, however, it is generally agreed that conjugation plays only a small part in the structure and behavior of butadiene. Instead, the shortness of the single C_2-C_3 bond can be attributed to hybridization, involving (more or less) sp^2 hybrid orbitals, with more *s* than *p* character to the orbitals (*1*):



The heat of hydrogenation is only 3.5 kcal per mole for the resonance energy of this molecule, indicating that only one pairing scheme is of major importance in butadiene, with very little contribution coming from resonance forms which have long bonds,



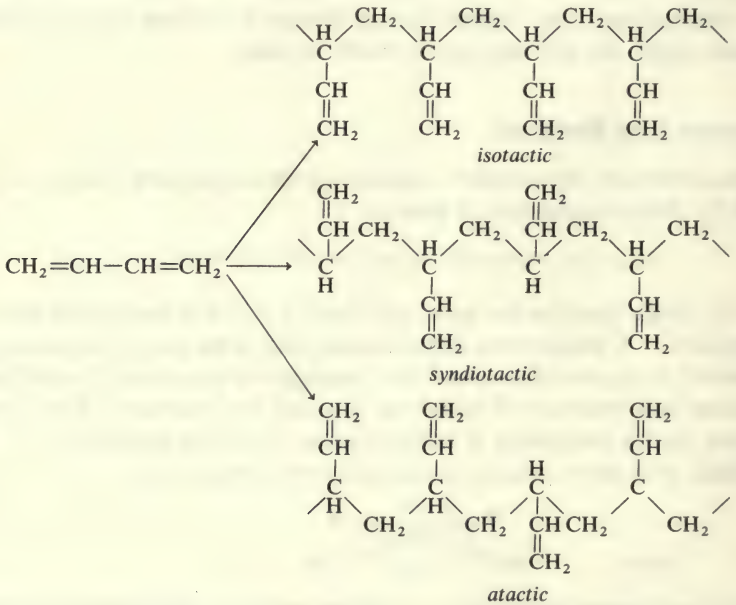
However, when a proton is added to butadiene, the resulting ion has two almost equivalent resonance forms, and its structure is a hybrid of the two,



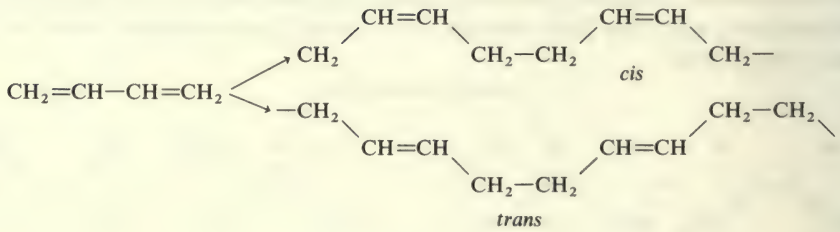
The earliest polymerization of this monomer was carried out by free-radical mechanism, using an emulsion technique. Shortly afterward, an anionic polymerization with sodium yielded a polymer that was an elastomer (*2*). This led to the eventual production of Buna rubber in Germany. Butadiene has since been polymerized in many ways, by various anionic and cationic catalysts and also by coordination catalysis.

Butadiene monomer can give rise to five distinct types of polymers. Of these there are three poly-1,2-butadienes, atactic, isotactic, and syndistactic, and two *cis* and *trans* forms of poly-1,4-butadiene:

Poly-1,2-butadiene:

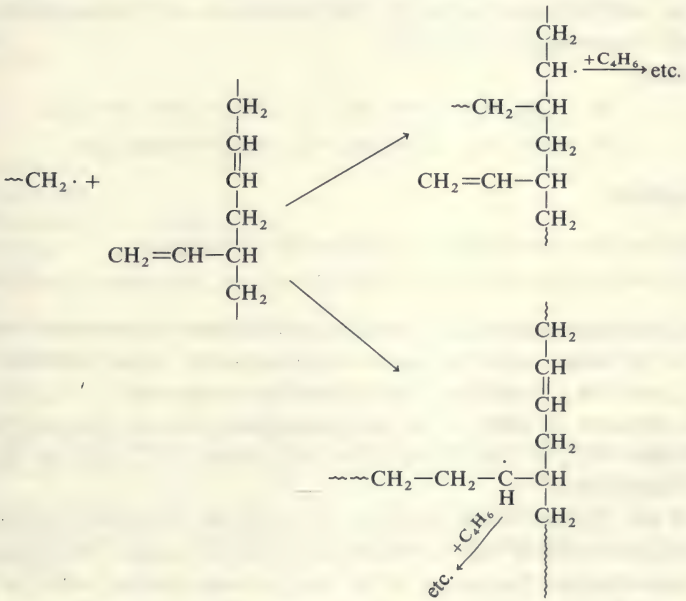


Poly-1,4-butadiene:



Free-radical polymerization of butadiene was shown to usually result in a polymer possessing 18–22% of the 1,2 adducts. This extent of the 1,2 units appears to be independent of the temperature of polymerization and results both from bulk polymerization and from emulsion polymerization. However, the ratio of *trans*-1,4 to *cis*-1,4 decreases with increase in the polymerization temperature. Thus at −20°C one can form 78% *trans*-1,4 units, but only 40% at 100°C.

Furthermore, free-radical polymerization of butadiene generally leads to polymers that are a mixture of 1,4 adducts and 1,2 atactic polymer, making them in effect copolymers of these polybutadienes. In addition, the residual unsaturation in the polymer chains can be a site for reactivity during the polymerization reaction, with the resultant formation of branching,



If such branching in polybutadiene becomes excessive, an infinite network may result, yielding a cross-linked, insoluble, and infusible material, often referred to as "popcorn" polymer. To avoid this, chain-transferring agents can be added to reduce chain length. This practice is in extensive use in emulsion copolymerizations of butadiene for the formation of Buna rubbers.

Ferrington and Tobolsky (*3*) investigated the cationic polymerization of butadiene with Lewis acids using $AlCl_3$ and related compounds as catalysts and carrying out the reactions at −78°C. Two types of polymers formed, a soluble and an insoluble one, with the amount of the insoluble one depending on the extent of conversion, and being present in greater amounts at higher conversions. $AlCl_3$, $AlBr_3$, and BF_3-Et_2O produced polymers of the same

structure, the ratio of *trans*-1,4 to the 1,2 adducts ranging from 4 to 5 when the polymerization was carried out in ethylene chloride solvent. $TiCl_4$ produced polymers with a somewhat lower ratio of *trans*-1,4 to 1,2 adducts. When the solvent was varied, the ratio 1,4:1,2 was also slightly varied. Addition of complexing agents such as nitroethane and nitrobenzene to the catalyst also caused variations in this ratio. These changes, however, were also small.

Anionic polymerization of butadiene has been accomplished in a variety of ways. "Alfin" catalysts (Chapter 6) can yield polymers of very high molecular weights, as high as 7,000,000 of high *trans*-1,4 structure (*4*). The rate of polymerization and the molecular weight of the product, however, are very sensitive to changes in the alkyl group of the organometallic and the alkoxide components of the catalyst.

The polymerization can also be quite readily initiated with metallic lithium as well as with lithium alkyls (*5*). The initiation and propagation steps are commonly represented as follows:

Initiation:

$$2Li + CH_2{=}CH{-}CH{=}CH_2 \rightarrow Li{-}CH_2{-}CH{=}CH{-}CH_2Li$$

$$LiR' + CH_2{=}CH{-}CH{=}CH_2 \rightarrow Li{-}CH_2CH{=}CHCH_2R'$$

Propagation:

$$Li{-}CH_2CH{=}CH{-}CH_2R'(Li) + n(CH_2{=}CH{-}CH{=}CH_2) \rightarrow$$

$$LiCH_2{-}CH{=}CH{-}CH_2{+}CH_2{-}CH{=}CH{-}CH_2{+}_{n-1}CH_2CH{=}CH{-}CH_2R'(Li)$$

When butadiene polymerization with butyl lithium is carried out in heptane, a product is obtained which possesses approximately equal amounts of *cis*-1,4 (48–58%) and the 1,2 addition, the remaining comprising 7–10% (*6*). Addition of small amounts of ether to the polymerization mixture changes the product to more than 80% of the 1,2 addition and about 10% each of the *cis*- and *trans*-1,4 additions.

Use of the Ziegler-Natta catalysts to carry out butadiene polymerization yields polymers with a high variation of 1,2 or 1,4 units. The composition is highly dependent on the nature of the catalyst and changes with the change in components. These variations were summarized in a table by Bawn and Ledwith in their review article (*7*). This is shown in Table 10-1.

So, as can be seen from the table below, it is possible to form almost all *cis*-1,4 (98%) and almost all *trans*-1,4 polybutadienes with the aid of coordination catalysis.

One catalyst of this type capable of yielding a high *cis*-1,4 adduct (98%) of butadiene was developed by Gippin (*8,9*), who used diethyl aluminum chloride and cobalt octoate. To activate it, the catalyst had to be modified somewhat by the addition of small amounts of oxygen or water. Gippin reported (*9*) that the most effective form of the Et_2AlCl–cobalt octoate catalyst is the one in which the diethyl aluminum exists in two states of relative Lewis acidity, Et_2AlCl and $EtAlCl_2$.

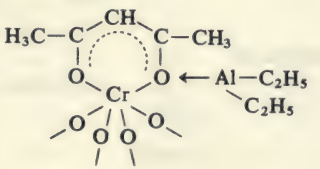
TABLE 10-1

Compositions of Polybutadiene Prepared with Coordination Catalysts[a]

Catalyst	Modes of addition, %		
	cis-1,4	*trans*-1,4	1,2
$TiCl_4$-AlR_3-Al:Ti < 1	6	91	3
$TiCl_4$-AlR_3-Al:Ti > 1	21–57	31–69	2–11
$TiCl_3(\alpha)$-$Al(C_2H_5)_3$	57	87	8
$TiCl_3(\beta)$-$Al(C_2H_5)_3$	37	60	3
$TiCl_3(\beta)$-AlR_2Cl	55–60	36–41	4
$TiBr_4$-$Al(C_4H_9)_3$	88	3	9
TiI_4-AlR_3	93–94	1.5–2	45–5
$CoCl_2$-AlR_2Cl	96–97	2.5	1–1.5
Co-stearate-AlR_2Cl	98	1	1
VCl_3-AlR_3	—	99	1
VOCl-AlR_3	—	97–98	2–3
VCl_4-AlR_3	—	97–98	2–3
$Ti(OC_4H_9)_4$-$Al(C_2H_5)_3$	—	0–10	99–100
V-(acetylacetone)$_3$-AlR_3			
V-(acetylacetone)$_3$-Al:V ~ 4 (unaged)	—	—	1–3
V-(acetylacetone)$_3$-Al:V ~ 10 (aged)	—	—	60
$MoO_2(OR)_2$-AlR_3			
Al:Mo < 6	—	—	75

[a] From Reference 7.

Bawn and co-workers (*10*) investigated butadiene polymerization with soluble coordination catalysts. They found that chromium acetylacetone and triethylaluminum will yield a predominantly 1,2-polybutadiene. The catalyst is a homogeneous complex, the structure of which was suggested by Sartoni and Costa (*11*) to be



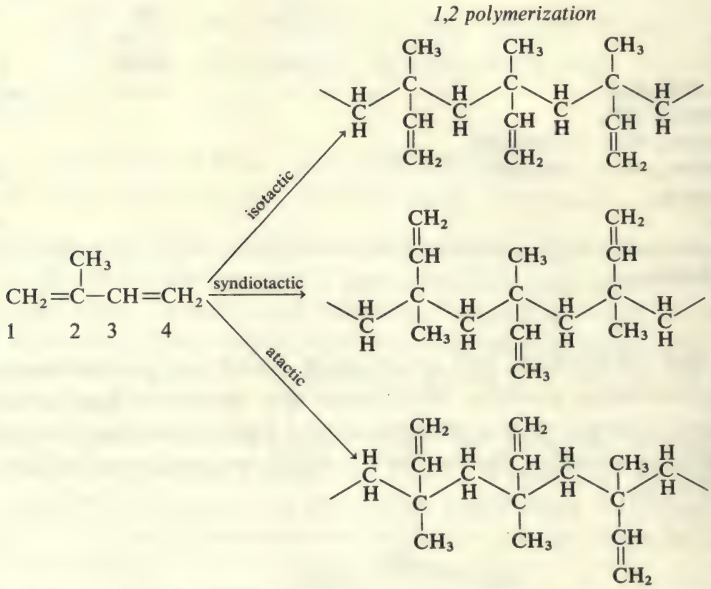
This complex contains two to six growing polymeric chains (*10*) per chromium atom and the propagation reaction exhibits kinetic behavior of simple bimolecular addition of monomer to an active center.

Rhodium salts, on the other hand, yield a predominantly *trans*-1,4 polymer. The reaction is accelerated by protonic acids, which include water, and by reducing agents capable of reducing $Rh^{\oplus\oplus\oplus}$ to $Rh^{\oplus}$ in aqueous systems.

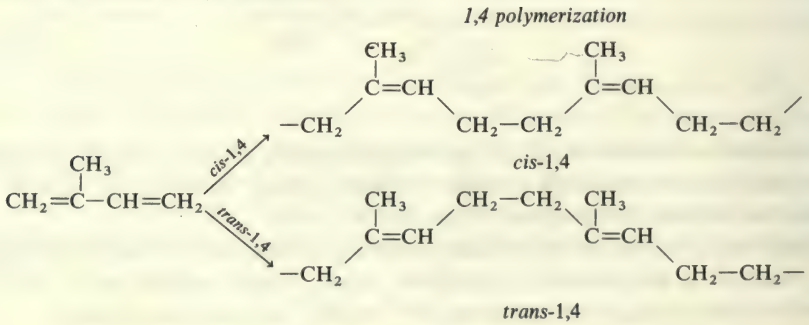
10-2. Polymers from Isoprene

The most common polymers from isoprene are the naturally occurring rubbers, which range in molecular weights from 200,000 to 500,000. These are found in at least 500 different species of plants, including trees, vines, and shrubs. The most important one is *Hevea brasiliensis*, which yields the all-1,4-*cis* isomer known as *hevea rubber*. The 1,4-*trans* isomer, known as *gutta-percha* or *balata*, is harvested from other plants. It lacks the resiliency and elastic behavior of natural rubber. The average molecular weight of gutta-percha is approximately 42,000–100,000. Both isomers show narrow-molecular-weight distributions, with natural rubber the most likely to be completely linear. The rubber is actually gathered from the tree in a form of a latex, a 25–40% emulsion stabilized by small amounts of protein and fatty acids.

Synthetic polyisoprene can potentially be in nine different forms. These are: (1) the three tactic forms of 1,2 addition:

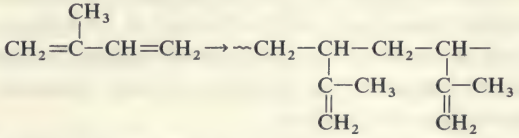


(2) the two forms of 1,4 addition:

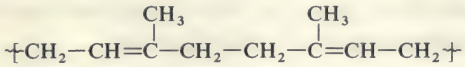


(3) the three 3,4 additions, also containing the atactic, isotactic, and syndiotactic forms:

3,4 polymerization



(all three forms are not shown) and (4) one random species possessing all the structures and perhaps in addition both head-to-head adducts and tail-to-tail adducts:



a head-to-head adduct

TABLE 10-2

Polymerization Products of Isoprene[a]

Mode of polymerization	% of adducts			
	cis-1,4	*trans*-1,4	1,2	3,4
Free-radical, emulsion	22.0	65.0	6.0	7.0
Cationic	36.7	50.6	3.8	8.9
Anionic, in pentane				
Lithium	94.4	0.0	0.0	5.6
Ethyllithium	94.2	0.0	0.0	5.8
Butyllithium	92.6	0.0	0.0	7.4
Sodium	0.0	43.0	6.0	51.0
Ethylsodium	6.3	42.0	7.1	44.6
Butylsodium	4.1	34.9	6.7	54.4
Potassium	0.0	52.0	8.0	40.0
Ethylpotassium	23.7	39.2	5.7	31.4
Butylpotassium	19.6	40.8	6.2	33.5
Rubidium	5.0	47.0	8.0	39.0
Caesium	4.0	51.0	8.0	37.0
"Alfin" (sodium)	27.0	52.0	5.0	16.0
Anionic, in diethyl ether				
Ethyllithium	6.0	29.1	5.3	59.6
Ethylsodium	0.0	14.3	10.2	75.6
Lithium	4.0	26.7	5.7	63.5
Coordination catalysis				
$TiCl_4$-AlR_3				
Al:Ti > 1	95	—	—	4
Al:Ti < 1	—	95	—	5
$TiCl_3(\alpha)$-Al(ethyl)$_3$	—	91	—	9
VCl_3-Al(ethyl)$_3$	—	99–100	—	—
V(acetylacetone)$_3$-Al(ethyl)$_3$	—	—	—	90

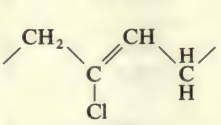
[a] From References *7* and *12*.

Various forms of addition which occur from the known methods of polymerization of isoprene are shown in Table 10-2. As can be seen from the table, when lithium-initiated polymerization of isoprene is carried out in a solvating solvent, the product has a high preponderance of 3,4 linkages. The same is true when the reaction is conducted in the presence of basic solvents such as amines. This is explained (Chapter 5) on the basis of ionic character and ionic radii of the alkali-metal-organo derivatives.

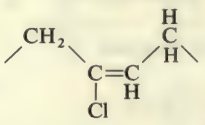
The significant thing, of course, is that now we have the means of preparing synthetic rubbers which are essentially duplicates of the naturally occurring polyisoprenes. As a result, some commercially available rubbers are quite similar to the natural *cis*-1,4 hevea rubber. These synthetic rubbers are processed and used in the same manner as natural rubber.

10-3. Polymers from Chloroprene

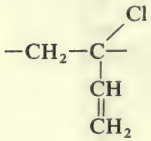
Just like isoprene, chloroprene can also be postulated to form nine different polymeric structures. Industrially this monomer is usually polymerized by free-radical mechanism in an emulsion system. As a result, most investigators are chiefly concerned with the presence of only four distinctive structures:



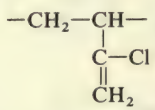
trans 1,4



cis 1,4



1,2 *adduct*



3,4 *adduct*

Maynard and Mochel (*13*) investigated chloroprene free-radical polymerization products with the aid of infrared analysis and concluded that the polymer structure is a function of the polymerization temperature. They carried out the polymerizations at temperatures ranging from -40 to $+100°C$, employing various free-radical initiators. Their results are shown in Table 10-3.

When polychloroprene was prepared cationically with aluminum chloride in ethyl chloride–methylene chloride mixtures at $-80°C$, the polymer was found to be about 50% 1,4 (*10*). Richardson and Sachar (*14*), who polymerized chloroprene with boron trifluoride, also found that this product was 50–75% a 1,4 adduct.

The commercial material (known as neoprene) is obtained by emulsion polymerization with typical free-radical initiators. The polymer has a molecular

TABLE 10-3

Structures of Polychloroprenes as a Function of Temperature of Polymerization[a]

Polymerization temp., °C	% 1,4 *cis*	% 1,4 *trans*	% 1,2	% 3,4
−40	5	94	0.9	0.3
−10	7	—	—	—
10	9	84	1.1	1.0
40	10	86, 81	1.6	1.0
50	11	—	—	—
80	—	—	2.0	2.1
100	13	71	2.4	2.4

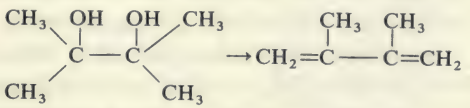
[a] From Reference *13*.

weight of 100,000 to 300,000. It swells but does not dissolve in benzene or hydrocarbon solvents. The material has a higher modulus of elasticity than natural rubber and is more resistant to oils. "Neoprene" rubber has a density of 1.23 and will undergo 800% elongation at the break.

10-4. Polymers from Other Dienes

Marconi and co-workers (*15*) reported stereospecific polymerization of 2-*t*-butyl-1,3-butadiene. This was accomplished with coordination catalysts based on $TiCl_4$ and aluminum alkyls or soluble aluminum hydride derivatives. Crystalline polymers resulted which melted at 106°C and were soluble in common solvents. X-ray data showed the polymers to have a *cis* configuration that distributes on three turns of a helical structure built on 11 monomeric units.

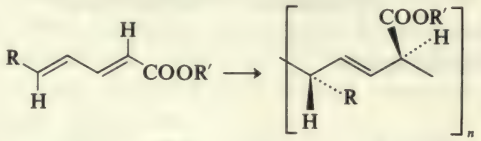
2,3-Dimethyl butadiene is another diolefin which may be used for the preparation of synthetic rubber. The monomer can be obtained readily by dehydrogenation of pinacol over alumina catalyst.



This diene can be polymerized by free-radical initiators or anionically with sodium to give so-called "methyl rubber." Coordination catalysts can also be employed to polymerize this monomer to a very high *cis*-1,4 polymer (*16,17*).

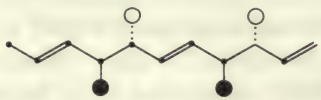
Natta and co-workers reported the preparation of isotactic substituted poly(carboxy butadienes) (*18–20*) with coordination catalysis. These were crystalline polymers obtained from alkyl esters of the *trans-trans* isomers of

sorbic acid and β-styrylacrylic acid. Such monomers, when polymerized 1,4, should yield the following recurring unit:



where R = CH_3; , and R′ = CH_3; C_2H_5; C_4H_9. With this recurring unit three potential sites for stereoisomerism were possible: at the double bond and at the two tertiary carbon atoms of the chain.

X-ray spectra of the polymers demonstrated a *trans*-isotactic configuration of the chains. From consideration of the mode of packing of these chains and from the encumberance of the side groups with regard to the main chain, Natta and co-workers (*18*) assigned an erythro configuration with respect to the relative placement of the lateral group. Thus the resultant polymers were tritactic and had a *trans*-erythroisotactic configuration:

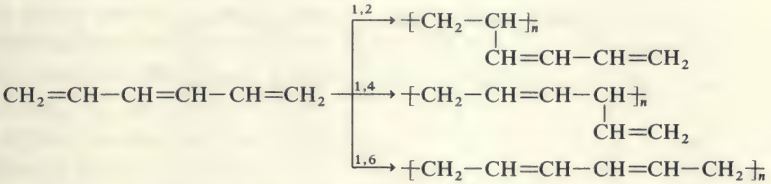


Two sites of isomerism are possible with polymers of 1,3-pentadiene (piperylene) per each monomer unit. This would mean that the number of stereoisomes possible for polypentadiene is higher than for polybutadiene or for polyisoprene. Also, pentadiene, owing to the presence of asymmetric carbon atoms in each 1,4 unit, can form three *trans*-1,4 and three *cis*-1,4 polymers (atactic, isotactic, and syndiotactic). Natta et al. reported (*21–25*) the preparation of *trans*-1,4 isotactic, *cis*-1,4 isotactic, and *cis*-1,4 syndiotactic polymers. He also prepared amorphous polymers which were predominantly *cis*-1,4 or *trans*-1,4 (*24*) but which lacked order in the configuration of the asymmetric carbon atoms.

The *cis*-1,4 syndiotactic polypentadienes were obtained with soluble cobalt catalysts. It is significant that only the *trans* isomer of pentadiene will polymerize with these catalysts and one can actually use a *cis* and *trans* mixture of the monomers with the *cis* isomer remaining unchanged by the reaction. The cobalt salt was used in conjunction with aluminum alkyl dichloride or aluminum dialkyl chloride. With the latter a Lewis base had to be employed to neutralize the cationic activity of the aluminum dialkyl chloride. This is due to the fact that pentadiene will polymerize with cationic initiators to low-molecular-weight polymers which are mainly 1,2 in structure. Natta and Porri also observed (*25*) that stereospecificity of the resultant product from these polymerizations depends strongly on the nature of the solvent. Thus *cis*-1,4 syndiotactic polypentadiene will form only in aromatic solvents, whereas in aliphatic solvents polymers will form with *trans* double bonds derived from 1,2 monomers.

10-5. Polymers from Trienes

When one considers the products from polymerization of conjugated trienes, a number of polymer structures are theoretically possible. Each of these structures should possess two residual double bonds, provided no secondary reactions take place. Thus hexatriene should potentially lend itself to three types of addition—1,2; 1,4; and 1,6 enchainment,



These structures would include, of course, all the *cis* and *trans* isomers.

Bell (*26*) studied conjugated triene polymerizations. He found that soluble coordination catalysts led to predominantly 1,6 enchainment. Thus stereospecific 1,6-polyhexatriene based on *trans-trans*-1,3-diene repeating units was prepared at low temperatures with vanadyl trichloride–triisobutylaluminum.

In addition, anonic polymerizations with butyl lithium in a tetrahydrofuran converted two hexatrienes, the *trans-trans*-1,3,5-heptatriene and the *trans-trans*-2,4,6-octatriene, into polymers that appeared to have nearly equal amounts of the following groups: vinyl, *trans-trans* dienes, *cis-trans* dienes, nonconjugated vinyls, and conjugated vinyls. An exception was polyoctatriene, which yielded no vinylic structures.

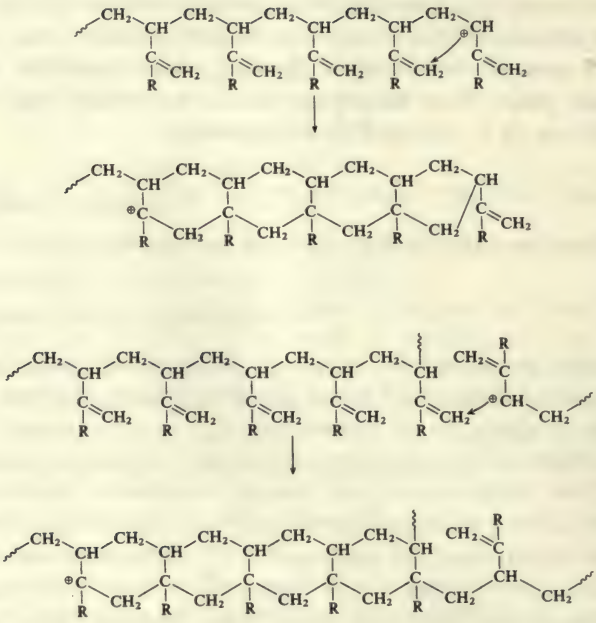
When free-radical emulsion polymerizations were carried out with potassium persulfate initiator on *trans*-1,3,5-hexatriene at room temperature over 48 hours, a white rubbery polymer formed. This elastomer had only a trace of vinyl groups present (*26*).

10-6. Cyclic Polymerization of Conjugated Dienes

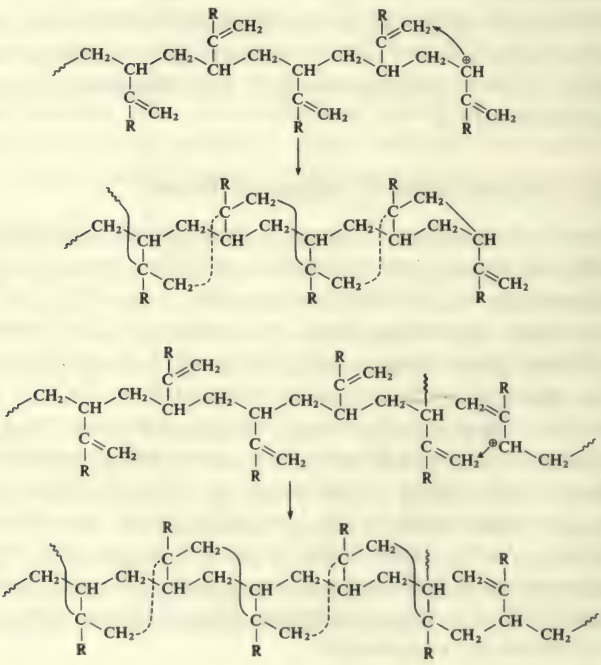
Gaylord and co-workers (*27*) reported that isoprene, butadiene, and chloroprene can be polymerized with complex catalysts consisting of alkyl or arylmagnesium bromide or triethylaluminum and excess $TiCl_4$ to form powdery, insoluble polymers possessing high heat resistance. The structures of these polymers differed from those usually obtained with catalysts prepared from higher molar ratios of organometallic compounds to $TiCl_4$.

It appears that this catalytic system led to predominantly 1,2 polymers in all three materials formed, which were then converted to ladder structures. The initial adducts were either 1,2-isotactic or 1,2-syndiotactic materials (3,4-isotactic or 3,4-syndiotactic in the case of isoprene and chloroprene) of the *trans* monomers. As the metal halide is present in excess, it was assumed (*27*) that the polymerization followed a cationic path. Two alternative mechanisms were preposed (*27*) for the cyclization, depending on whether the starting polymer is isotactic or syndiotactic:

Mechanism A:



Mechanism B:



10-7. Copolymers of Conjugated Dienes

Many copolymers of the conjugated dienes are known and some are of considerable industrial importance. This is particularly true for butadiene-styrene copolymers (*28–30*), which have been worked on since World War I. The German chemists were the first to prepare a useful synthetic rubber (Buna-S) through the copolymerization of butadiene and styrene in 75:25 ratios using emulsion polymerization techniques. The reaction was initiated with persulfates, and mercaptans were employed as chain-transferring agents to regulate chain length and branching. This original technology was enhanced and refined in the United States during World War II. Here the copolymer (GR-S) was prepared at lower molecular weights, in order to be able to employ equipment used with natural rubber at ordinary temperatures. A typical recipe, by parts [many variations of which are available (*31*)] is as follows: butadiene, 75; styrene, 25; dodecyl mercaptan, 0.5; water, 180; potassium persulfate, 0.3; and soap, 5.0.

The reaction takes place for approximately 14 hours at 50°C, at which time 78% conversion is reached. The mercaptan acts as a reducing agent as well as a chain-transferring agent, so a redox initiation takes place. Upon completion of the reaction period, the reaction mixture is quenched with hydroquinone, the unreacted volatile butadiene removed, and the copolymer latex precipitated by an acid salt solution.

Later a "cold rubber" process evolved, in which the reaction is carried out at anywhere from −10 to 0°C. A redox system active at these low temperatures, such as *p*-menthane hydroperoxide, and ferrous ions is employed. Rubbers formed by this process exhibit better working qualities than the original GR-S rubbers and are less branched. The emulsion copolymers of butadiene are high in *trans*-1,4 adducts of butadiene. The molecular weights of these rubbers range from 25,000 to 500,000.

At the time of development of the Buna-S rubber in Germany, a more oil-resistant analog, Buna-N, evolved. Here styrene was replaced by acrylonitrile in very similar formulations. Butadiene is also used in ratios of 75:25 to acrylonitrile. The reactivity ratios of the two monomers are such that at the early stages of conversion, the amount of acrylonitrile in the copolymer is high, but this high incorporation of acrylonitrile decreases as the reaction proceeds toward completion. To obtain more uniform incorporation of monomers, continuous-monomer-feed type of polymerizations are often employed. The GR-N rubbers are less flexible at lower temperatures than natural rubber.

During World War II considerable effort was spent in the United States on the manufacture of synthetic rubbers with the aid of "alfin" catalysts. These were copolymers derived from butadiene, isoprene, or piperylene with styrene. The high-*trans* polymers were hard to process, however, because the molecular weight ranged from 5 to 10 million and perhaps even higher, although "alfin" rubbers had many very desirable properties.

Recently, a successful application of molecular-weight regulators was reported by Hansley and Greenberg (*32*). These are dihydro derivatives of benzene and naphthalene which are capable of reducing molecular weights of the "alfin" polymers to 200,000–350,000 without altering their microstructures. As a result, it should be possible to prepare a wide series of polymers and copolymers with predetermined molecular weights and composition within the same plant. Specifically, "alfin" polybutadiene with limited amounts of styrene would be a solution-type SBR.

The anionic copolymerization of conjugated dienes with styrene is interesting in that although the rates of homopolymerization of such monomers decrease in the order styrene, isoprene, and butadiene, the rate of their copolymerization is reversed and now becomes butadiene, isoprene, and styrene.

This inversion effect was investigated by Spirin and co-workers (*33,34*), who employed ethyllithium as the catalyst. They found that when the copolymerization is carried out in toluene, r_1 (isoprene) = 0.5 and r_2 (styrene) = 0.25. However, when a Lewis base is present in the reaction mixture, r_1 (isoprene) = 1.0 and r_2 (styrene) = 0.8.

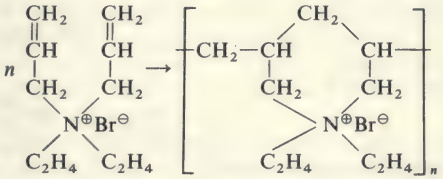
Korotkov and co-workers (*35*) studied copolymerization of isoprene-styrene and butadiene-styrene with *n*-butyllithium with respect to composition of copolymers formed in hydrocarbon solvents and their reaction kinetics. They observed that the reaction is a "living"-chain type of copolymerization of isoprene and styrene in which blocks of desired length and different composition can be formed. They also noted that although styrene is a more active monomer in homopolymerizations than butadiene, in copolymerizations styrene is the more active of the two. This reversal of activity they ascribed to more favorable steric factors in the interaction of butadiene molecule with active centers (the frequency factor being three orders higher than that for styrene). Kunz (*36*) postulates it as being due to the formation of π-complexes between the monomer and the organometallic compound.

In benzene, or in bulk, *n*-butyllithium and ethyllithium will give butadiene copolymers containing about 20% styrene. In triethylamine, diethylether, and in tetrahydrofuran, however, the initial copolymers contain 60, 68, and 80% styrene, respectively. Once again this demonstrates that the composition of the copolymer is mainly a function of the ionic character of $C^{\ominus}M^{\oplus}$ ion pair (Chapter 5).

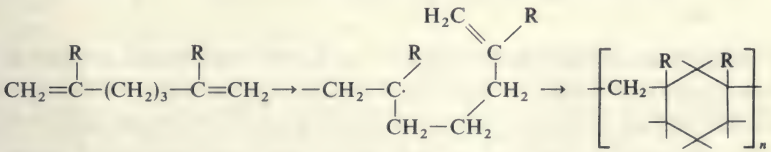
Both *n*-butyllithium and lithium metal will give copolymers of isoprene which are composed 80% or more of the *trans*-1,4 adduct when conversions are low. At higher conversions, however, the per cent *cis*-1,4 content increases at the expense of *trans*-1,4. When an ionizing solvent such as diethylether or tetrahydrofuran is employed, or when sodium is used as the catalyst in place of lithium, more or less random mixtures of 3,4- and *trans*-1,4 structures are produced. This, of course, is in line with results obtained on isoprene homopolymerization.

10-8. Polymers from Nonconjugated Dienes

When nonconjugated dienes are polymerized by a free-radical mechanism, the most expected products are cross-linked polymers (*37*). In spite of that, Butler and Angelo formed soluble polymers from diethyldiallyl ammonium bromide (*38*) which he believed to be the result of an "alternating intermolecular-intramolecular" reaction which results in producing recurring piperidine units,



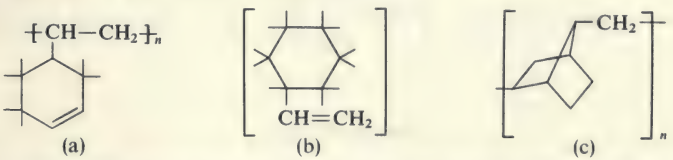
Marvel and Vest expanded this to formation of a six-membered carbon ring by polymerizing three 2,6-disubstituted 1,6-heptadienes by a free-radical mechanism (*39*),



where R = $Co_2C_2H_5$, CO_2CH_3, or CO_2H.

These diolefins polymerized readily in bulk, solution, and emulsion systems. The products were soluble in chloroform and benzene. Infrared data indicated a complete absence of unsaturation in the products.

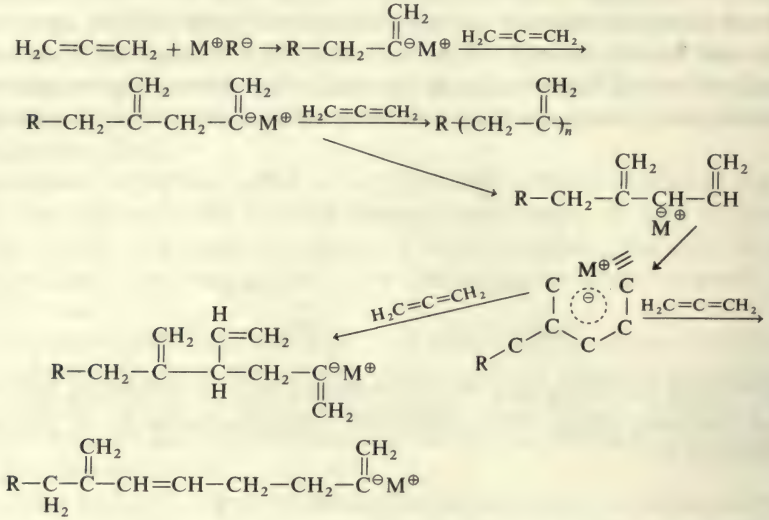
Butler and Miles (*40*) used cationic and Ziegler catalysts to study the polymerization of a 1,5-diene,4-vinylcyclohexene. Cationic mechanism led to 28% conversion to form a polymer, 85% of which was soluble. Roughly half of the soluble polymer contained cyclic structures. The Ziegler catalysis led to a product of which 45% was soluble and essentially saturated, structure (c). This product was quite crystalline. Three types of adducts appear possible. Structure (c) was the saturated, highly crystalline material:



(a) (b) (c)

Baker investigated the action of the coordination catalysts on the polymerization of cumulene, an allene (*41*). He employed Ziegler catalysts, which were transition-metal salts reduced by aluminum triisobutyl. The products contained three types of unsaturation: vinylidine, vinyl, and *cis*. No *trans* unsaturation

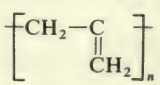
was found. Baker hypothesized the following mechanism to explain the path of the reaction:



The polyallene chains when examined by X rays were found to exist in three different crystalline forms as well as in an amorphous form. Although Baker (*41*) did not obtain a regular structure, Otsuka and co-workers apparently did (*42*). They managed to form 1,2-polyallene by using π-complexes of nickel, such as bis(1,5-cyclooctadiene) nickel, or $(\pi\text{-}C_8H_{12})_2Ni$; bis($\pi$-allyl) nickel, or $(\pi\text{-}C_3N_5)_2Ni$; π-allylnickel bromide, or $(\pi\text{-}C_3H_5NiBr)_2$; and bis(acrylonitrile) nickel, or $(CH_2CHCN)_2Ni$. They concluded that the divalent nickel complexes were inactive and that the low valency states of nickel were the important electronic structures for the catalyst.

They also found that if nickel acetylacetonate was reduced with triethyl aluminum, a cross-linked polymer resulted. Cobalt complexes also appeared to yield insoluble polymers, and iron pentacarbonyl failed to polymerize allene at 40°C. The same is true of triiron dodecacarbonyl.

The polymer structure obtained with the nickel complexes appears to be, at least in its major part, a regular repeating sequence of



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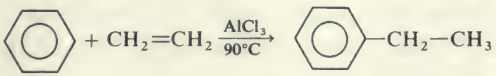
11

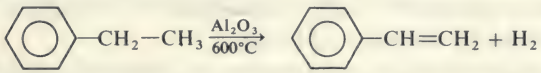
Styrene and Styrene-Like Polymers and Polyacrylics

11-1. Polystyrene

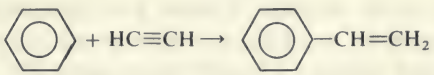
The monomer, phenyl ethylene or vinyl benzene, can be prepared in a variety of ways, such as condensing benzene with acetylene, or with ethylene. In the United States, ethylene is used because it is cheapest. The Friedel-Crafts reaction is carried out over $AlCl_3$ at approximately 90°C to form ethyl benzene in the initial step:



The ethyl benzene is then dehydrogenated over alumina catalyst at 600°C:



One-step condensation of acetylene and benzene to yield styrene is another alternative:



Over the past 30 years, styrene polymerization has been the source of much scientific research and many publications. The first polystyrene appears to have been prepared by Simon (*1*). Free-radical polymerization of styrene can be carried out by bulk, solution, suspension, or emulsion techniques. Stobbe and Posnjak demonstrated (*2*) that styrene polymerizes by free-radical mechanism more slowly in the dark than it does in the presence of light. Staudinger and co-workers (*3,4*) investigated free-radical polymerization of styrene quite thoroughly and demonstrated that polymers of various molecular weight sizes can be obtained readily, depending upon the conditions of polymerization

used. Furthermore, Schulz demonstrated that conditions of polymerization can also affect the microstructure (*5*). Thus polymers prepared at low temperatures were essentially linear, whereas those prepared at higher temperatures appear branched, particularly when high initiator concentrations were used.

Commercially styrene is often polymerized in bulk to form castings. If particularly large castings are desired, this is usually done in layers to avoid heat buildup and resultant bubble formation. Such free-radical bulk polymerizations may be completed at elevated temperatures. Emulsion polymerizations of styrene have the disadvantage of yielding a polymer that possesses poor optical clarity.

Polystyrene prepared by free-radical mechanism is atactic (T_g = 80°C), composed of head-to-tail sequences. Styrene can also be polymerized by various cationic and anionic initiators as well as with the aid of coordination catalysis.

Natta (*6,7*) prepared isotactic polystyrene with the aid of aluminum alkyls and titanium halide complexes. This preparation was advanced further by Overberger (*8*) and Shelyakov (*9*) to yield convenient methods for laboratory syntheses.

Isotactic polystyrene was shown by Natta (*6,7*) to be composed of head-to-tail sequences, the main chain being helical with three monomer units in each helical fold.

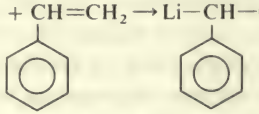
Morton and Grovenstein (*10*) were the first to demonstrate that styrene can be polymerized by organometallic compounds. Kern et al. (*11*) further showed that catalysis by amylsodium will yield isotactic polystyrene which matches the isotactic polystyrene prepared by Natta (*6,7*). Other alkali organometallic compounds, such as triphenylmethylpotassium (*12*) and "alfin" catalysts (*13*), are also capable of yielding stereospecific polystyrene. The above initiators yield such stereospecific polymers under heterogeneous conditions. One can also obtain these polymers using homogeneous conditions, by employing lithium organometallic initiators (*14,15*).

The kinetics of polymerization of styrene by *n*-butyllithium in benzene and in hexane containing less than a 1:1 ratio of tetrahydrofuran to *n*-butyllithium was investigated by O'Driscoll and Tobolsky (*16*). Their results indicated that monomeric *n*-butyllithium initiates styrene polymerization in benzene and that termination occurs by association between the propagating anion, the lithium counterion, and another *n*-butyllithium molecule:

Initiation:

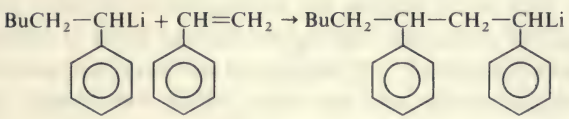
$$(BuLi)_6 \rightleftharpoons 6BuLi$$

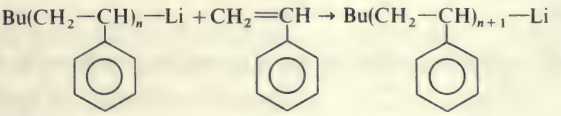
$$BuLi + CH{=}CH_2 \rightarrow Li{-}CH{-}CH_2{-}Bu$$



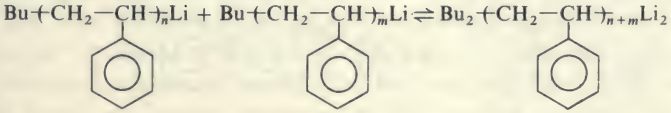
This view was also taken by Cubbon and Margerison (*17*), although they proposed a termination mechanism that involves association between two propagating chains:

Propagation:





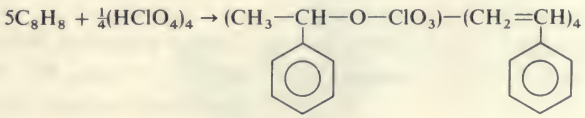
Termination:



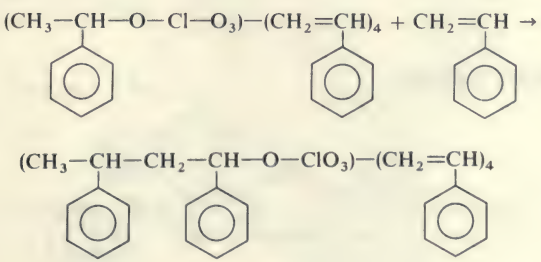
Morton (*18*) has produced considerable evidence for this mechanism.

As mentioned earlier, styrene lends itself readily to polymerization by cationic mechanism as well. Lewis acids are typical catalysts for such polymerizations, although other electrophilic materials often exhibit some catalytic activity. But, when perchloric acid is used as initiator in methylene chloride or dichloroethane solvent, there is doubt that the mechanism is truly cationic. Gandini and Pleash reported that polymerization actually proceeds normally in the absence of carbonium ions (free or paired) and that the chain carriers are 1-phenylethyl perchlorate and the analogous oligomeric ester, a likely product from reaction of styrene and perchloric acid (*19–21*). They postulate that this "pseudocationic" polymerization proceeds as follows:

Initiation:

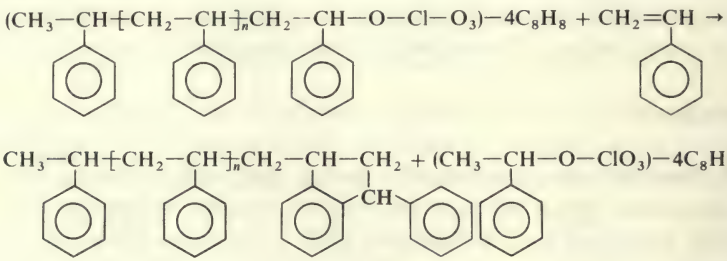


Propagation:

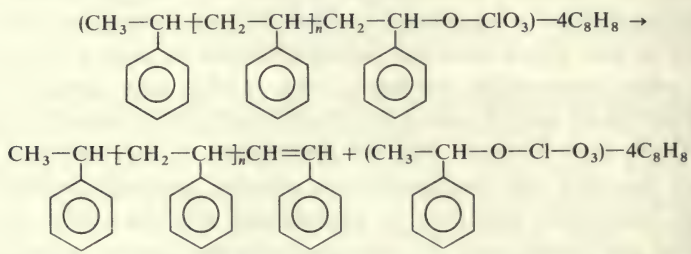


The presence of double bonds and indanyl end groups was observed by means of spectroscopy. This could explain the mechanism of transfer, which appears important, as the DP in this reaction is low. So two types of transfer reactions were proposed as taking place: one dependent on monomer concentration and giving rise to indanyl groups and the other, which was termed "independent transfer," which gives rise to double bonds:

Monomer transfer:

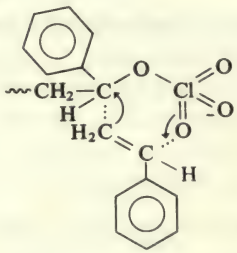


Monomer-independent transfer:

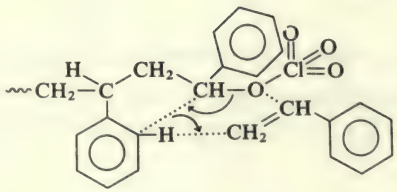


The mechanism of propagation and transfer reaction is explained on the basis of cyclic transition states:

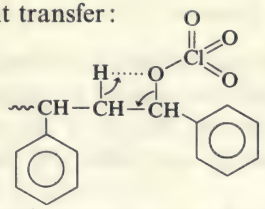
For propagation:



For monomer transfer:



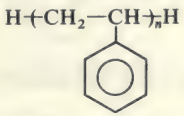
For monomer-independent transfer:



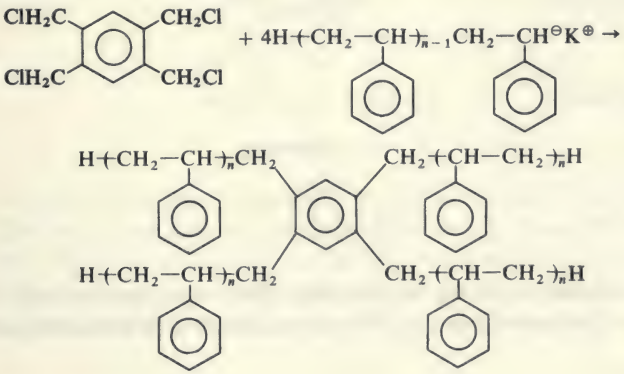
The above mechanism contradicts one proposed by Pepper and Reilly, which is based on a more conventional interpretation and which utilizes the concept of formation of carbonium ions (*22*).

Because styrene is a common and interesting vinyl monomer which lends itself to polymerization by various mechanisms, efforts were made to prepare monodisperse polystyrene. The earlier work was done by Bianchi and co-workers (*23*), who controlled the growth of styrene radicals in an emulsion polymerization by means of successful additions of overwhelming amounts of initiator radicals at regular intervals. This was accomplished with intermittent ultraviolet light, which was employed to decompose azobisisobutyronitrile initiator present in the reaction mixture, thereby causing formation of a large population of initiating radicals at regular intervals. A high-molecular-weight polymer resulted, with relatively narrow-molecular-weight distribution.

Since then a number of monodisperse linear polystyrenes were prepared by anionic mechanism (*24–26*). In addition, attempts were made to form trifunctional star molecules from polystyryllithium coupled with 1,2,4-trichloromethylbenzene (*27*) by Wenger and Yen. In a recent paper, Yen (*28*) reported preparation of a virtually monodisperse polystyrene ($\overline{M}_w/\overline{M}_n = 1.06$) by using α-phenylethyl potassium as the initiator. The chain was terminated with a proton so that the product was effectively an ideal polystyrene molecule,



He was also able to form a virtually monodisperse polystyrene tetrafunctional star molecule ($M_w/M_n = 1.05$) by coupling of polystyrylpotassium with 1,2,4,5-tetrachloromethyl benzene (*28*),



11-2. Copolymerization of Styrene

Styrene can be copolymerized by free-radical mechanism with a vast number of monomers (*29*). Such copolymerizations are possible either in bulk, solution, suspension, or emulsion systems. Some of the more common copolymers include those with acrylonitrile, acrylates and methacrylates, maleates and fumarates, and others.

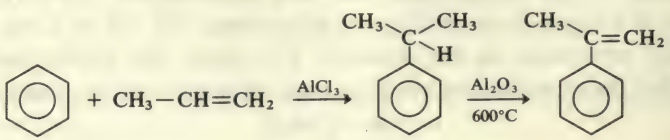
Generally, copolymers of styrene and acrylonitriles (as well as methacrylonitrites) possess higher heat-distortion temperature, higher tensile strengths, and greater elongation than styrene homopolymers.

The introduction of acrylates and methacrylates into polystyrene chains leads to increased weatherability and generally higher softening points. Some acrylates, however, like butylacrylate, lower the T_g of polystyrene (*30*). On the other hand, introduction of small amounts of methacrylic acid groups will raise the softening point slightly and lower the elongation (*31*).

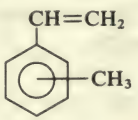
Finally, styrene can also be copolymerized with many monomers with the aid of ionic and coordination catalysis, yielding either random or block copolymers, depending upon the specific catalyst used.

11-3. Derivatives of Styrene

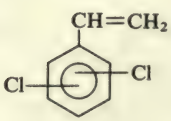
Some of the most common derivatives of styrene include *α-methyl styrene*, which can also be prepared with the aid of the Friedel-Crafts reaction,



vinyl toluene (the commercially available material appears to be a mixture of *meta* and *para* isomers),

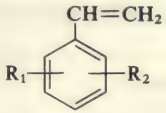


and *dichlorostyrene*,



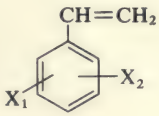
Other substituted styrenes are known. They were synthesized at various times and their polymers formed. We can put them into three categories:

1. Alkyl- or aryl-substituted styrenes:



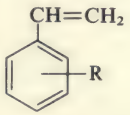
where R_1 and R_2 are alkyl or aryl groups.

2. Halogen derivatives:



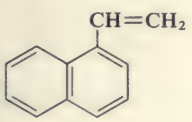
where X_1 and X_2 are Cl, Br, I, and F.

3. Polar-group-substituted styrenes:

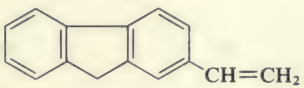


where R = $-C\equiv N$; $-CHO$; $-CO_2H$; $-O-CO-CH_3$; $-OH$; $-OCH_3$; $-NO_2$; $-NH_2$; and $-SO_3H$.

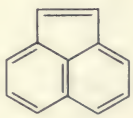
In addition, other monomers similar to styrene, which can be polymerized in a manner similar to it, are known. Some of these are



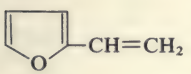
1-vinyl naphthalene



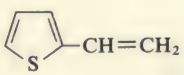
2-vinyl fluorene



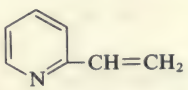
dehydroacenaphthene



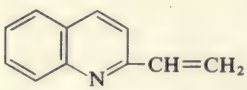
α-vinyl furan



α-vinyl thiophene



2-vinyl pyridine



α-vinyl quinoline

Vinyl toluene will polymerize at 100°C by the free-radical mechanism at a greater absolute rate than styrene, the activation energy being 17–19 kcal per mole, vs. that for styrene, 21 kcal per mole. All known systems for polymerization such as mass, solution, emulsion, and suspension can be used to polymerize vinyl toluene. This is not true, however, for α-methyl styrene, as the allylic

TABLE 11-1

Melting Points of Some Isotactic Phenylalkanes

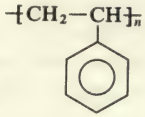
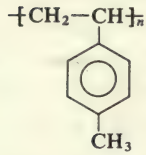
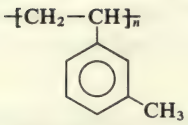
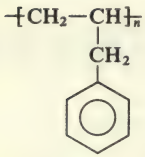
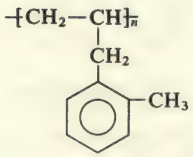
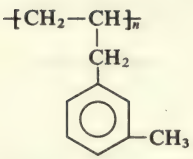
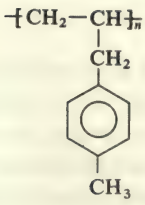
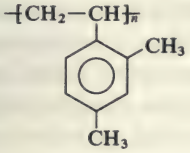
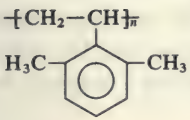
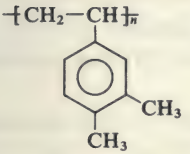
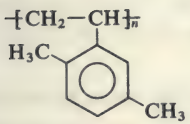
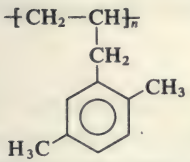
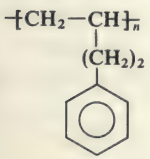
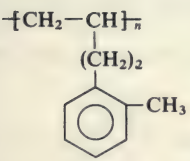
Repeating units	Glass (*Tg*)	m.p.,°C (*Tm*)	Ref.
		240	*39*
		Amorphous	*39*
		215	*39*
	60	207–208	*40*
	80	290	*40*
	35–40	180	*40*
	60–65	240	*40*

Table 11-1 *(continued)*

Repeating units	Glass (*Tg*)	m.p.,°C (*Tm*)	Ref.
		310	*39*
		330	*39*
		240	*39*
		290	*39*
		334–338	*40*
	10	162–168	*40*
		234–239	*40*

character of the methyl group prevents formation of high-molecular-weight polymers by the free-radical mechanism.

Natta and co-workers studied the polymerization of α-methyl styrene by coordination catalysis (*32,33*) but failed to form a polymer. Sakurada found (*34*), however, that polymerization can be achieved with $TiCl_4$-$Al(C_2H_5)_3$ at $-78°C$ with the activity of the catalyst and the DP, depending on the ratio of the aluminum alkyl to titanium halide, as well as on the mixing and aging of the catalyst and the nature of the solvent. The optimum ratio of $Al(C_2H_5)_3$ to $TiCl_4$ appeared to be 1.0:1.2. At ratios higher than 2.0 the reaction did not proceed. The mixing and aging of the catalyst had to be carried out below room temperature. The valence state for titanium had to be maintained between 4 and 3. From the comparison of results, he concluded that the reaction proceeded by cationic mechanism and that the active catalytic species was the intermediate complex $[(TiCl_3)^{\oplus}Al(C_2H_5)_2Cl^{\ominus}]$, with the reaction product being $Al(C_2H_5)_2Cl$.

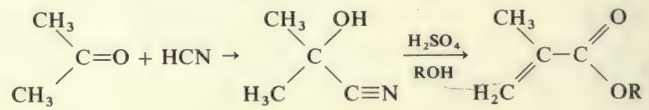
Cationic polymerization of α-methyl styrene to low-molecular-weight polymers was achieved earlier with the use of metal halides (*35–37*). The products were either largely unsaturated (*37*) or saturated (*36*) and possessing phenylindane terminal groups.

The best cationic polymerization conditions to achieve a high-molecular-weight product require low temperatures (between -90 and $-130°C$) and Lewis acid catalysts, such as aluminum chloride (*38*). Ethyl chloride or carbon disulfide are suitable solvents for such reactions. The products have narrow-molecular-weight distributions.

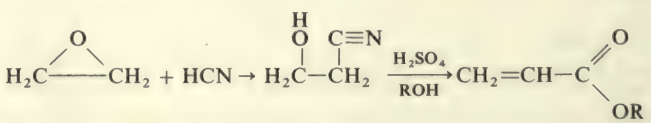
The melting points of a number of isotactic polyphenylalkanes can be found in the works of Natta (*39*) and Price and co-workers (*40*), who carried out studies on the influence of substituents on physical properties of these materials. Some of that information is shown in Table 11-1.

11-4. Acrylates and Methacrylates

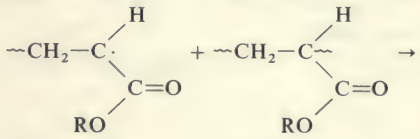
The commonly used monomer synthesis is based on the cyano-hydrin formation from acetone to prepare methacrylate esters:



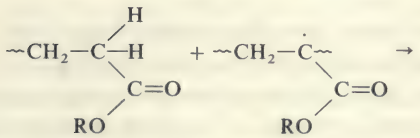
The acrylate esters can be formed just as readily by condensing hydrocyanic acids with ethylene oxide:



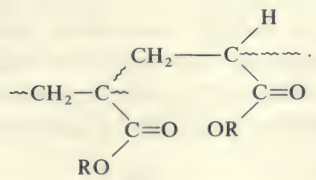
The acrylate and methacrylate esters can be polymerized readily by free-radical mechanism when free-radical initiators, heat, or light are employed. When the acrylates are polymerized in bulk, they show a characteristic rapid acceleration in rate at low conversions. This is accompanied by formation of cross-linked polymers and by very high molecular weight of that portion of the formed polymer which is still soluble. Fox and Gratch (*41*) explain this by suggesting that cross-linking occurs through a chain-transferring mechanism which involves abstraction of a labile hydrogen from a "dead" polymer chain. This results in growth of a branch radical:



"dead" polymer



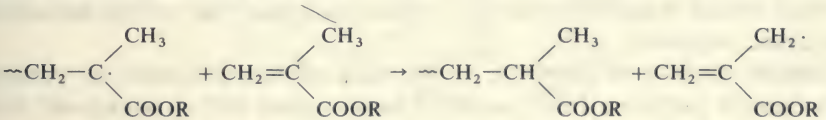
new "dead" polymer *new polymer radical*



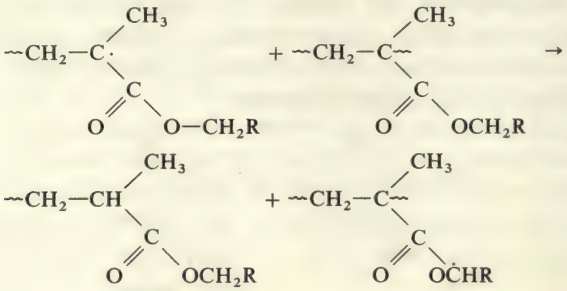
branch radical

All terminations of branch radical chains by combination will result in formation of cross-linking of two polymers. Such a process probably occurs with many other vinyl monomers. With acrylates, the greater tendency to form gelation by this process may be the result of attaining higher molecular weights. This is confirmed by the fact that addition of chain-transferring agents, such as mercaptans (which reduce primary chain lengths), tends to prevent gel formation.

Such chain transferring, to form gels in bulk polymerization, which leads to gels, is not possible in the methacrylates, as they lack the labile α-hydrogen. The growing radical can abstract a proton from the α-methyl group in a different chain-transferring process:



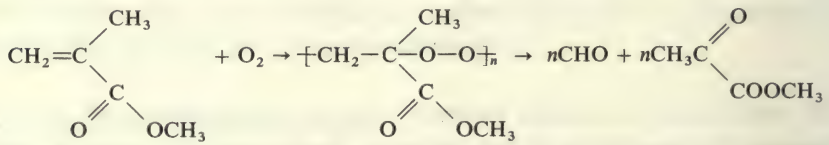
This reaction, however, does not appear to be very important in polymerization of the methacrylates (*42*). It does not mean that cross-linked or gelled polymethacrylates will not form in bulk polymerization. Such polymers have actually been prepared. Their formation, however, is explained (*43*) by chain transferring occurring with the alcohol alkyl group of the polymer,



Presumably gelation will then occur by combination of two branch radicals.

The termination reaction in the polymerization of the acrylic and methacrylic esters is believed (*43*) to occur by both disproportionation and recombination. In the case of methyl methacrylate, it has been demonstrated to occur predominantly by disproportionation when the polymerization is carried out at 25°C (*42*).

Oxygen was shown to inhibit free-radical polymerization of methyl methacrylate (*44*). Furthermore, low-molecular-weight polymeric peroxides will form in a reaction between methyl methacrylate and oxygen (*45*) which will then decompose to formaldehyde and methyl pyruvate,



Oxygen has undoubtedly an inhibiting effect on acrylate polymerizations as well, although less work appears to have been carried out to study this reaction. Melville did demonstrate, however, that oxygen reacts 400 times more rapidly with a methacrylate radical than it does with an acrylate radical (*46*).

Wiley and Brauer (*42*) determined the T_g's of the various atactic polyacrylic and polymethacrylic esters. They are shown in Table 11-2. The solubility in oils and hydrocarbons increases with the increase in the length of the ester side chain in both polymers, the acrylates and the methacrylates.

Ionic polymerization of acrylic and methacrylic esters can only be carried out with the aid of anionic initiators, as these monomers fail to lend themselves to cationic initiation.

Lithium alkyls were shown to be the most efficient initiators for yielding stereospecific polymers from α-methyl methacrylate (*47*) as compared to a

TABLE 11-2

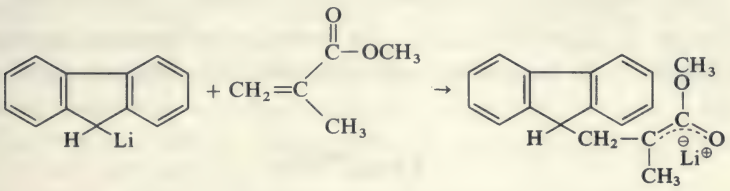
Glass Transition Temperature of Atactic Acrylic and Methacrylic Esters[a]

Polyacrylates	*Tg*, °C	Polymethacrylates	*Tg*, °C
Methyl	3	Methyl	105
Ethyl	−23	Ethyl	47
n-Propyl	−51.5	*n*-Propyl	33
n-Butyl	−70	*n*-Butyl	17
n-Tetradecyl	−20	*n*-Octyl	−70
n-Hexadecyl	35	*n*-Decyl	−70
		n-Tetradecyl	−9

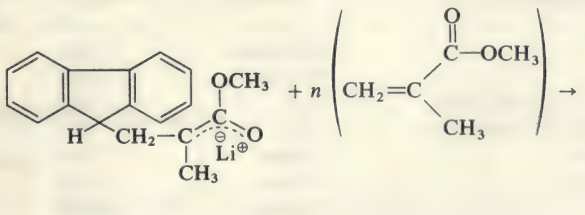
[a] From Reference *42*.

number of other organometallic compounds. Glusker and co-workers (*47,48*), who studied these reactions, concluded that the probable mechanism of initiation is by a Michael addition across the carbon-carbon double bond of the monomer, leaving the alkyl or aryl fragment of the organometallic initiator chemically bound to the end of the polymer chain. This agrees well with the mechanism shown in Chapter 5. Thus, when 9-fluorenyl lithium was used for initiation, fluorenyl groups were found at the terminal ends:

Initiation:



Propagation:



The strong ultraviolet absorption of fluorenyl groups was used to calculate number average molecular weights. This agreed with osmotic-pressure measurements. It enabled Glusker and co-workers (*47,48*) to demonstrate that one fluorenyl group did indeed become chemically attached to each chain, thereby substantiating the reaction mechanism.

Furthermore, they also demonstrated that the termination reactions in these polymerizations, which involve carbanionic chain ends, are likely to be very slow or nonexistent. This was shown by the fact that terminations with ^{14}C-labeled carbon dioxide or tritium-labeled acetic-acid-produced radioactive polymers. A comparison of the resultant radioactivity with the fluorenyl content showed that in polymerizations which reached a high degree of conversion, 80–100% of the chains could still be made radioactive. Glusker and co-workers (*48*) concluded that chains of different steric configurations may propagate at different rates even in a homogeneous medium.

When anonic polymerizations are carried out with organolithium initiators (*n*-butyllithium or 9-fluorenyllithium) in hydrocarbon solvents, isotactic poly(methyl methacrylate) can be formed (*49*). When a solvent of medium polarity is used, blocks of isotactic and syndiotactic copolymers of poly(methyl methacrylate) result. But when a strongly polar solvent such as glycol dimethyl ether is used, a syndiotactic poly(methyl methacrylate) forms. Goode et al. (*50*) demonstrated that the ability of ethers to influence stereospecificity can be related to their Lewis-base strength:

tetrahydrofuran > tetrahydropyran > dioxane > diethylether

Korotkov et al. also found (*51*) that isotactic poly(methyl methacrylate), m.p. 150–160°C, can be prepared with organolithium initiators in toluene, but

TABLE 11-3

Anionic Polymerization of *t*-Butyl Acrylate[a]

Catalyst	Solvent	Yield, %	Crystallinity, %
n-BuLi	Ethyl ether	52.2	39.9
n-BuLi	Toluene	81.1	29.2
Disodium trinaphthyl boron	THF	48.2	50.8
Dipotassium benzophenone	THF	46.3	43.0
n-BuLi-Et_3Al	Toluene	37.0	19.5
n-BuLi-Et_2Cd	Toluene	92.5	—
Li-$CdEt_3$	Toluene	100.0	70.2
Li-$ZnEt_3$	Toluene	89.8	29.0
NaH-$ZnEt_2$	Toluene	92.3	40.6
Sr-$ZnEt_4$	Toluene	82.9	61.3
Ca-$ZnEt_4$	Toluene	100.0	60.0

[a] From Reference *54*.

TABLE 11-4

Catalysts Useful in Anionic Polymerization of Methyl Methacrylate[a]

Catalyst	Polymerization temp., °C	Solvent
$BuLi\text{-}AlEt_3$	−70	Ether or toluene
$BuLi\text{-}ZnEt_2$	−70	Ether
$BuLi\text{-}CdEt_2$	−70	Ether or toluene
$EtMgBr\text{-}AlEt_3$	−70	Hexane or toluene

[a] From Reference *54*.

in liquid ammonia or pyridine a syndiotactic polymer, m.p. 190–200°C, forms instead.

Gall and McCrum (*52*) also reported preparation of syndiotactic poly(methyl methacrylate) using sodium dispersion in hexane. The reaction was initiated at 40°C and then carried out at 20–25°C over a 24-hour period to obtain 60–65% conversion.

When calcium hydride–triethyl amine was used in combination with $LaAlH_4$, an isotactic polymer resulted. Use of $LiAlH_4$ alone, on the other hand, yielded a stereoblock polymer (*52*).

As a result of numerous research efforts, many crystalline polymeric acrylates and methacrylates were reported. Thus, for instance, Miller et al. (*53*) prepared crystalline polyacrylic acid by first forming crystalline poly(*t*-butylacrylate) with lithium dispersions and then hydrolyzing the product with HCl. The same catalytic system (*52*) led to other crystalline polyacrylates (such as methyl, *n*-butyl, *s*-butyl, and isobutyl).

Tsuruta and Furukawa (*54*) summarized the catalysts for anionic polymerizations of *t*-butyl acrylate in a table. This is shown as Table 11-3. They also listed catalysts useful for anionic polymerization of methyl methacrylate. These are shown in Table 11-4.

11-5. Related Acrylic Polymers

Polyacrylonitrile

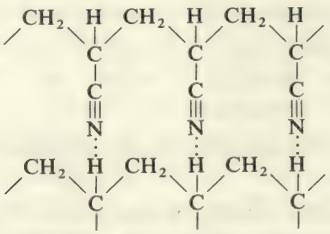
The monomer, acrylonitrile, is usually prepared commercially by either dehydration of ethylene cyanohydrin with the aid of catalysts,

$$CH_2\!\!\diagup\!\!\diagdown\!\!O\!\!\diagdown\!\!\diagup\!\!CH_2 \xrightarrow{HCN} CH_2(OH)-CH_2CN \xrightarrow{200\text{–}350} CH_2{=}CH{-}C{\equiv}N + H_2O$$

or through condensation of acetylene with HCN over cuprous chloride,

$$HC{\equiv}CH + HCN \xrightarrow[H_2O]{CuCl_2} H_2C{=}CH{-}C{\equiv}N$$

The monomer can be polymerized readily by free-radical mechanism. The polymer is insoluble in the monomer and tends to precipitate out. The same is true for polymerization in most solvents with the exception of dimethylformamide. The structure of the polymer is such that hydrogen bonding can form quite easily. This contributes to the strength of the polymer, making it also poorly soluble in many solvents and giving it a high softening point.

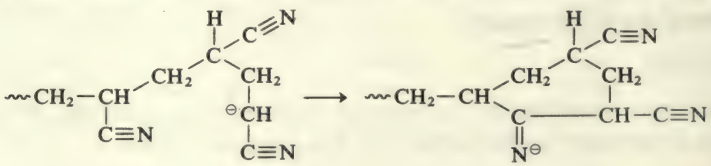


Methacrylonitrile is quite similar in properties to acrylonitrile and can be polymerized just as readily.

Anionic initiators, such as sodium in liquid ammonia, Grignard reagents, or triphenylmethyl sodium, will yield high-molecular-weight polymers at low temperatures (*55*). On the other hand, cationic initiators will not polymerize acrylonitrile. In fact, Lewis acids were reported to form stable complexes with the monomer (*56*). Some studies originally seemed to have indicated that under certain conditions, acrylonitrile polymerizations could be initiated by cationic mechanisms, but this now appears to have been free-radical in nature, involving oxygen (*57,58*).

Complexes with zinc chloride can radical polymerize through the vinyl group and also through the nitrile group (*59*). The polymerization of the nitrile group, however, is not straightforward when there are hydrogens situated α to the nitrile.

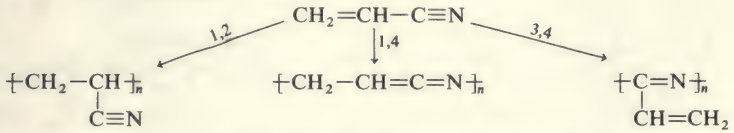
Evans observed (*60*) that anionic polymerization of acrylonitrile does not proceed to completion at temperatures above 50°C. This he explains on the basis of monomolecular rearrangement which prevents further chain growth.



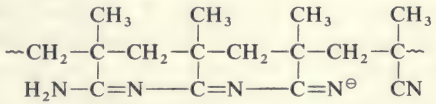
However, at lower temperatures, Zilkha and Avery obtained high-molecular-weight polymers at high conversions with higher monomer concentrations (*61*). The termination occurred by transfer to monomer (see Chapter 5). The termina-

tion reaction actually depends upon catalyst concentration. Thus Ottolenghi and Zilkha (*62*) demonstrated that at high catalyst concentration, termination is by chain transfer to monomer and at low concentration it is by internal cyclization.

Generally, anionic initiation of acrylonitrile or methacrylonitrile can lead to three different modes of addition (*63,64*),



The 3,4 addition can also lead to formation of a ladder structure if it takes place after, or simultaneously to 1,2 addition,

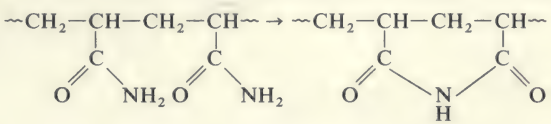


Polyacrylamide

The monomer can be formed readily through the reaction of ammonia with acrylic acid or acrylic esters and by reduction of acrylonitrile. The monomer will polymerize occasionally with considerable violence upon melting. It can also be polymerized in a water solution to form water-soluble polymers (*65*). Free-radical polymerization in solvents will usually lead to relatively low molecular weight polymers.

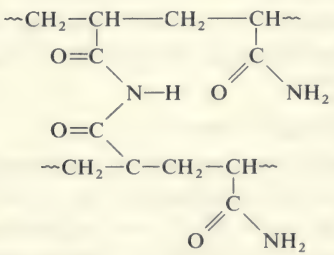
Thermal polymerization of acrylamide is possible in bulk at 150°C (*66*). But this leads to two types of imidization,

1.



or

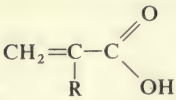
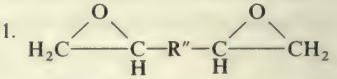
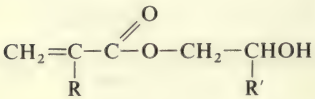
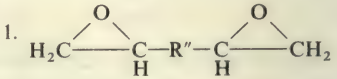
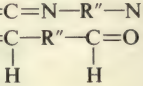
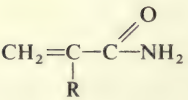
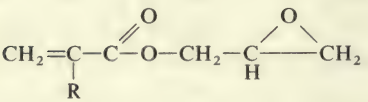
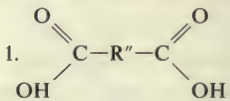
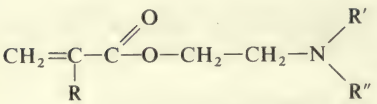
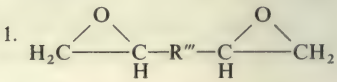
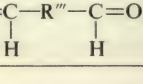
2.



Crystalline poly(N,N′-disubstituted acrylamides) were prepared by Attfield (*67*) with butyllithium and ethyllithium in hydrocarbon solvents. The melting

TABLE 11-5

Acrylic Monomers Containing Functional Groups

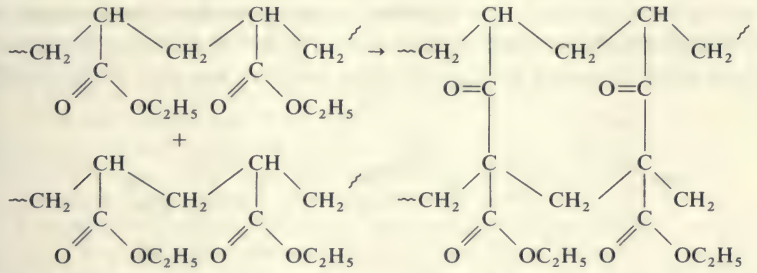
Monomer	R and R′	Cross-linking agent
	H; CH_3	1.  2. Aminoplasts 3. O=C=N—R″—N=C=O
	H; CH_3	1.  2. Aminoplasts 3. O=C=N—R″—N=C=O 4. 
	H; CH_3	1. Formaldehyde 2. Reaction 1 + epoxy resins 3. Aminoplasts
	H; CH_3	1.  2. anhydrides 3. amines
	H; CH_3 R″=CH_3; $C(CH_3)_3$	1.  2. O=C=N—R‴—N=C=O 3. 

points of some of the tactic polyacrylamides were found to be considerably higher than the atactic isomers. Thus atactic N,N′-diisopropyl acrylamide melts at 100–125°C, whereas the isotactic analog melts at 170–200°C. The syndiotactic *n*-isopropylacrylamide melts at 170–200°C, whereas the amorphous analog melts at 100–125°C.

Polymers from Polyfunctional Monomers

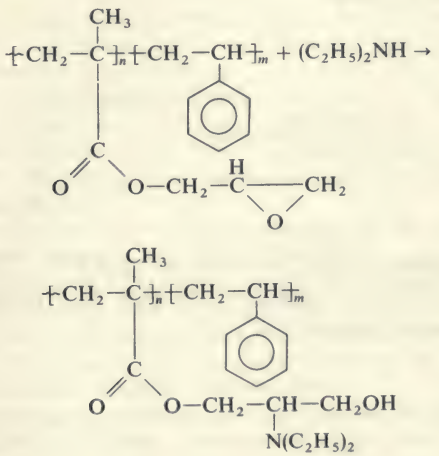
Acrylic and methacrylic esters have been copolymerized with a great number of monomers by free-radical mechanism. In general, the suitability of copolymers for use in special applications is related to their molecular weights and their T_g's. Because many of the acrylic and methacrylic ester copolymers are used in coatings, difunctional monomers were developed to facilitate cross-linking. This is outside the ability of polymers prepared from monofunctional

acrylates to cross-link by the mechanism of a Claisen condensation. Such reactions are, in fact, utilized commercially to cross-link or "vulcanize" polyacrylic elastomers.

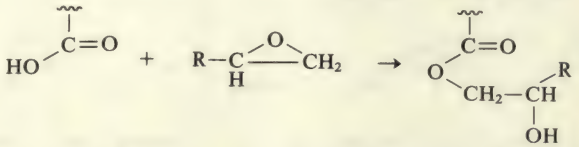


What is being referred to here, however, are acrylic monomers which possess, in addition to the olefin, other reactive groups to be used for subsequent cross-linking, after relatively low molecular weight prepolymers are first prepared by free-radical polymerization of the acrylate or methacrylate portion of the monomer. Such monomers will possess either carboxyl groups, hydroxyl groups, amide groups, or epirane groups. An allylic double bond can also be introduced. So, upon polymerization, or, more commonly, copolymerization, the polymer backbone contains such pendant groups, which can then be subjected to a variety of reactions. Table 11-5 presents such acrylic monomers, possessing secondary functional groups and the cross-linking agents commonly used for thermosetting their prepolymers.

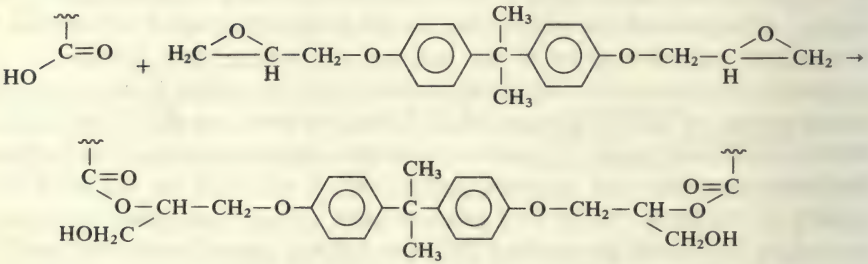
Kelly et al. (*68*) reported on a general study of thermosetting vinyl and acrylic copolymers. Epoxy-, carboxyl-, and amido-substituted acrylic copolymers were prepared by copolymerizing glycidyl methacrylate, acrylic acid, and acrylamide, respectively, with styrene in a conventional free-radical solution process. In addition, copolymers of glycidyl methacrylate were treated with diethyl amine to form hydroxyl groups,



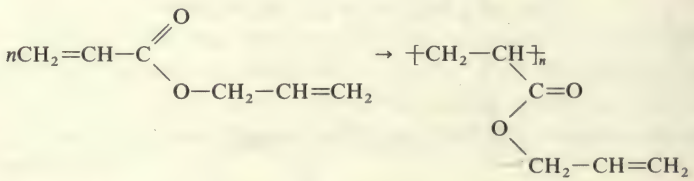
Also, an acrylic acid copolymer was heated under reflux with butylene oxide in the presence of a basic catalyst. This second method was used to esterify a vinyl toluene–acrylic acid–acrylamide copolymer, which was subsequently treated with *p*-formaldehyde. The resulting hydroxy-methylolamide copolymer was able to intercondense when heated at 120°C for 30 minutes. When cross-linking took place via epoxy groups, the basic reaction was that of esterification,



Thus



It is interesting to note that Donati and Farina (*69*) formed a crystalline polymer from allyl acrylate, a difunctional monomer. The polymer was prepared under homogeneous conditions in toluene at −50°C with either butyllithium or phenylmagnesium bromide. The reaction proceeded without gel formations to conversions greater than 70%. Infrared spectra of the polymer indicated that all additions took place through the acrylate double bond and none through the allyl group,



The resulting polymer melted between 86 and 90°C. The most interesting aspect of this work was the apparent absence of cyclopolymerization (*67*), which might have been expected.

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12

Halogen-Bearing Addition Polymers and Vinyl Esters and Ethers

12-1. Poly(vinyl chloride)

The monomer, vinyl chloride, is usually prepared from acetylene and hydrochloric acid,

$$HC{\equiv}CH + HCl \xrightarrow[HgCl_2]{100\text{–}250^\circ C} H_2C{=}CHCl$$

It can, of course be prepared by other means. The monomer can be polymerized quite readily by free-radical mechanism, preferably at lower temperatures, owing to instability of the polymer, which tends to decompose by losing HCl,

$$\sim CH_2{-}\underset{Cl}{CH}{-}CH_2{-}\underset{Cl}{CH}\sim \xrightarrow{\Delta} \sim CH{=}CH{-}CH_2{-}\underset{Cl}{CH}\sim + HCl$$

Oxygen acts as a retarder in free-radical vinyl chloride polymerizations. Commercially, poly(vinyl chloride) homopolymers and copolymers are usually prepared by emulsion and suspension polymerizations. A number of poly(vinyl chloride) copolymers are also prepared in solution.

The kinetics of polymerization of vinyl chloride in bulk (*1*), using a peroxide catalyst at 25–50°C, indicate that the reaction rate tends to increase over the first 40% of polymerization, then remains constant from 40 to 60%, and then gradually decrease as complete conversion is approached. On the other hand, Jenckel et al. (*2*) found that in the presence of benzoyl peroxide, vinyl chloride polymerization at 50°C exhibits an induction period and then is linearly accelerated with time until 80–90% conversion is reached. At that point, the reaction slows down, and the last 1–2% of vinyl chloride is very difficult to polymerize.

Danusso and Perugini (*3*) noted that vinyl chloride, when pure, will not polymerize in the absence of an initiator, but the presence of only trace amounts is sufficient to effect polymerization.

The homopolymer is essentially a head-to-tail adduct and probably branched through chain transferring. The solid polymer is only slightly crystalline, the crystallite being rather smaller than usually found in other polymers.

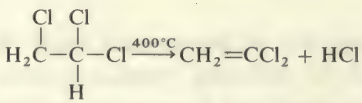
Syndiotactic poly(vinyl chloride) was prepared by Fordham and co-workers (*4*) and Rosen and co-workers (*5, 6*) by carrying out the polymerizations at low temperatures (−40 to −15°C) with organoboron initiators. Such reactions are known to proceed by free-radical mechanism (*7–9*) but lead to steric control, because of low temperatures.

Yamazaki and co-workers (*10*) investigated vinyl chloride polymerization with complex catalysts made up of titanium (tetra-*n*-butoxide)-aluminum alkyl chloride. This was an attempt to carry out stereospecific polymerization of vinyl chloride by coordination catalysis without addition of nucleophiles (see Chapter 6) (*11, 12*). They found that use of aluminum ethyl dichloride in place of aluminum diethyl chloride enhanced the catalyst reactivity. Also, the presence of halogenated hydrocarbons accelerated the polymerization rate. The polymer yields depended upon the mole ratios of Al to Ti, the maximum being at about 1.7 for both $AlCl(C_2H_5)_2$ and $AlCl_2(C_2H_5)$. The authors presented evidence that the reaction mechanism was probably not a free-radical one, but rather a coordinated one, yielding a syndiotactic polymer.

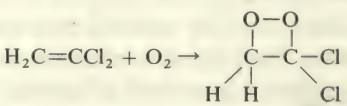
Poly(vinyl chloride) can be further chlorinated to contain 60–65% chlorine by weight. This tends to improve the solubility and toughness of the polymer as well as its heat stability.

12-2. Poly(vinylidine chloride)

Vinylidine chloride monomer is prepared commercially by thermal cracking of trichloroethane,



The monomer reacts quite readily with oxygen to form peroxides,

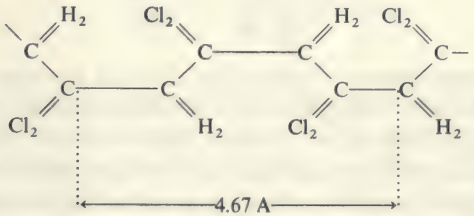


These peroxides are known to decompose explosively. The monomer lends itself to free-radical polymerization by all known techniques, including bulk. However, bulk polymerization on a large scale is hard to control, so industrially the homopolymer is usually prepared by emulsion or suspension polymerization.

In poly(vinyl chloride) the monomer units as stated are largely in a head-to-tail arrangement. The carbon-chlorine bonds are oriented in a random fashion in relation to chain zigzag. And, the hologens, because of their size, hinder

rotation around the carbon-to-carbon single bond with the result that the sequences are quite rigid at room temperature.

In poly(vinylidine chloride), on the other hand, the polymer molecules were shown by X rays (*13*) to exist in regular structures,

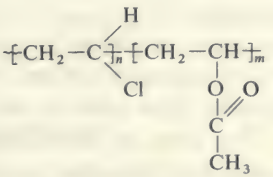


As a result, the homopolymer is quite crystalline, T_m = 160°C. The crystallinity ranges from 20 to 40%. The polymer is insoluble in the monomer and at molecular weight above 100,000 in most solvents at room temperature, and only with difficulty in chlorinated solvents at elevated temperatures.

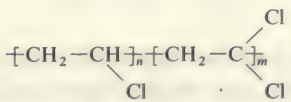
12-3. Copolymers of Vinyl Chloride and of Vinylidine Chloride

Many copolymers of both monomers are known and used commercially. Perhaps the most important (commercially) copolymers of vinyl chloride are those with vinyl acetate. These range from a few to 40% of vinyl acetate in composition. They are also available over a wide range of molecular weights to suit various needs. The copolymerizations are carried out either by emulsion, suspension, or solution methods.

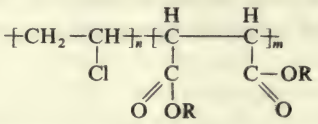
The copolymers have a lower softening point than the homopolymers, better solubility, and heat and light stability,



Another common type of copolymer of vinyl chloride is that with vinylidine chloride. These copolymers have greater tensile strength than the copolymers of vinyl chloride with vinyl acetate,



Copolymers of vinyl chloride with a number of esters or half-esters of maleic and fumaric acids are also available commercially,

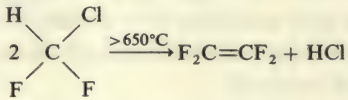


Many different copolymers of vinylidine chloride are also known. Besides those with vinyl chloride, copolymers of vinylidine chloride with acrylonitrile and with methacrylonitrile have received attention (*14*). These copolymers were shown to possess the best combination of properties of either monomer as well as fairly high melting points, when the ratios of the two monomers in the copolymers were approximately equal.

It is interesting that whereas the reactivity ratios of methyl methacrylate and vinylidine chloride are $r_1 = 2.53 + 0.01$ and $r_2 = 0.23 + 0.03$ at 60°C, respectively, copolymers of these two monomers can be formed. A copolymer of the two monomers which possesses 42% methyl methacrylate is soluble in dioxane and has a relatively low fusion point.

12-4. Polytetrafluoroethylene

The monomer tetrafluoroethylene is synthesized by the condensation of difluorochloromethane,

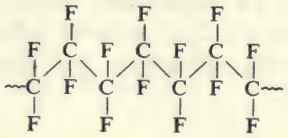


This reaction is usually carried out in an electric furnace and results in good yields of the monomer. Oxygen can cause an explosive polymerization of tetrafluoroethylene and even detonate it.

Commercially, the polymerization reaction is commonly carried out at elevated temperatures with a redox initiation system. Persulfates and hydrogen peroxide are two types of initiators often used. In such reactions, the heat of polymerization is quite high. This must be controlled, as the monomer may undergo a simultaneous rearrangement and cleavage at elevated temperatures (explosively),

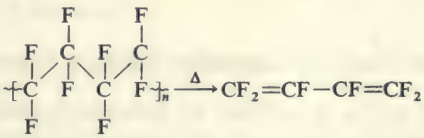
The polymer is believed to be completely linear and is highly crystalline. The linearity of the polymer can be attributed to the carbon-fluorine bond

strength, which is not readily ruptured by chain transferring. So we can show the structure in this manner:



Two crystalline forms of the polymer, both helical, are known. The high form consists of 15 CF_2 groups per unit cell. The low form consists of 13 CF_2 groups per unit cell and apparently transforms above 19°C to the high form. T_m of this polymer is 327°C and T_g is below −100°C. The molecular weight of polytetrafluorethylene is hard to establish because of poor solubility, but it is estimated to be quite high, probably in the millions.

On pyrolysis, polyperfluoroethylene decomposes to hexafluorobutadiene as well as other degradation products, such as dimers and monomers (see Chapter 25),



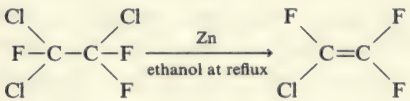
The physical properties of this macromolecule depend mainly on crystallinity, molecular weight, and void content.

Polytetrafluoroethylene will not flow even above its melting point. This is explained as being caused by restricted rotation around the C—C bonds and also due to high molecular weight. This restricted rotation also appears to cause considerable stiffness of the chain of the solid polymer, as it was observed that the C—F bonds in polytetrafluoroethylene are 1.42 A, whereas the bond distance of *gem* difluorides should be 1.35 A.

Polytetrafluoroethylene is insoluble in most solvents, with the exception of perfluorinated kerosene, in which it is soluble at 300°C.

12-5. Polychlorotrifluoroethylene

The monomer chlorotrifluoroethylene can be prepared by removing two chlorine atoms from trichlorotrifluoroethane with zinc,



This monomer, which boils at −28°C, is quite toxic. Its polymerization is accomplished by a free-radical mechanism, using an emulsion polymerization

technique with a redox-type initiator. The polymer is inert chemically and has a high melting point (218°C), but these properties are somewhat inferior to those of polytetrafluoroethylene. This is probably due to a lower degree of symmetry. Polychlorotrifluoroethylene can be quenched to form clear amorphous sheets. In addition, polychlorotrifluoroethylene will dissolve in many solvents at temperatures above 100°C.

12-6. Poly(vinyl fluoride) and Poly(vinylidine fluoride)

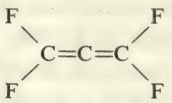
The monomer vinyl fluoride boils at −88°C. Polymerization is accomplished by free-radical mechanism, usually at high pressures. The polymer is quite similar to poly(vinyl chloride), although much more crystalline, harder, and more rigid, owing to the strong carbon-fluorine bond. It also exhibits good heat stability.

Poly(vinylidine fluoride) is also a hard, crystalline polymer which is brittle. The monomer vinylidine fluoride is a gas that will polymerize by free-radical mechanism at high pressures.

12-7. Miscellaneous Fluorine-Containing Addition Polymers

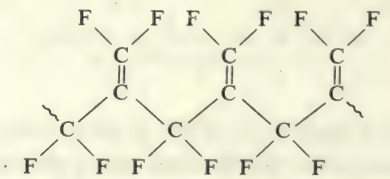
Over the last 15 years, a number of fluorine-containing monomers were prepared and polymerized in search of special properties, such as high heat stability and good chemical inertness. Among these might be mentioned the perfluoalkyl propenyl ketones, reported by Rausch and co-workers (*15*). The monomers, prepared by the Grignard reaction, exhibited polymerization reactivities similar to those of other β-substituted α,β-unsaturated ketones.

Another interesting monomer is tetrafluoroallene, reported by Jacobs and Bauer (*16*). The monomer



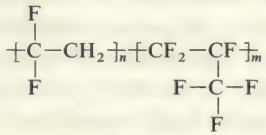
prepared from dehydrobrominating 1,3-dibromo-1,1,3,3-tetrafluoro-propane, is a colorless gas, boiling at −38°C.

Tetrafluoroallene polymerizes at room temperature under autogenous pressure to form a waxy powder. The powder is insoluable in most solvents and highly crystalline. On the basis of X-ray data, the following structure was assigned:



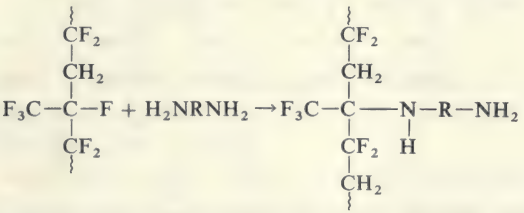
12-8. Copolymers of Fluorine-Containing Monomers

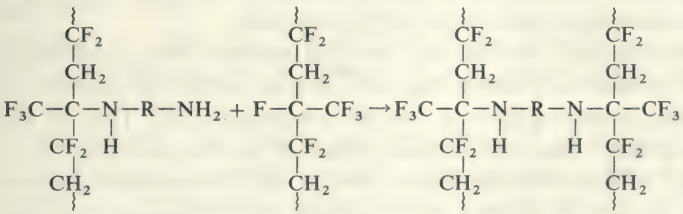
A useful commercial elastomer is a copolymer of vinylidine fluoride and hexafluoropropylene (*17*),



The r values of the two monomers are quite different. Actually, hexafluoropropylene does not homopolymerize. Nevertheless, copolymerization is achieved and generally conducted under emulsion polymerization conditions, with persulfate initiators and bisulfite reducing agents. Other redox systems can be employed as well. Molecular weights as high as 150,000 are obtained.

The copolymer is an elastomer, whereas the poly(vinylidine fluoride) homopolymer is rigid and brittle. The introduction of the hexafluoropropylene groups into the polymer chains breaks up the symmetry and produces elasticity. The elastomer can be cross-linked with peroxides or with polyfunctional amines in the following manner:



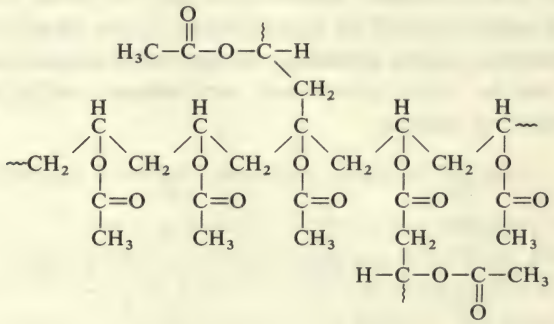


12-9. Poly(vinyl esters)

Vinyl acetate monomer may be formed quite readily by reacting acetylene with acetic acid. The reaction can be conducted either in the liquid or in the vapor phase (*18*). In the liquid phase, the reaction can be catalyzed by complex mercury salts and sulfuric acid at temperatures from 30 to 90°C. Zinc acetate over charcoal support can be used as the catalyst for the vapor-phase reaction at 180°C,

Free-radical polymerizations of vinyl acetate are carried out quite easily, but although the vinyl acetate radical is very reactive, the monomer is relatively unreactive. This results in a greater tendency to copolymerize than to homopolymerize. Furthermore, this leads to a very considerable tendency to chain-transfer and to branch-formation. So polymerizations must be conducted with a fairly pure monomer to obtain high molecular weights. Also, bulk polymerizations can usually not be carried out to 100% conversion, as the chain transferring and branching will eventually lead to gelation.

Chemical investigation of the polymer (*19*) showed that the additions are almost all head to tail. The branching occurs both at the α-carbon on the acetate group or on the tertiary carbons along the polymer backbone (α-vinyl carbon). These occur through the mechanism of abstraction of hydrogen by the vinyl acetate radicals,



As one can expect, the polymers are amorphous and atactic (T_g = 40°C). The lower-molecular-weight species are soft and gummy.

X-ray data obtained on poly(vinyl alcohol) prepared from poly(vinyl acetate) showed it to be atactic, whereas that obtained on poly(vinyl alcohol) prepared from poly(vinyl formate) showed it to be syndiotactic (*20*). This led to several studies on regularity and steric arrangements of the two polymers (*21*, *22*). The two polyvinyl esters are readily hydrolizable to the corresponding polyalcohols. Presence of 1,2 glycols among such alcohols would indicate that tail-to-tail placement occurred during polymerization, for such glycols could not have formed in any other manner. It was found that the amount of tail-to-tail addition which occurred in poly (vinyl acetate) was not a function of the surrounding medium (*21*), whereas in poly(vinyl formate) the placement was strongly influenced by electrostatic factors.

Fujii and co-workers (*21*) suggested, therefore, that interaction between formyl groups of poly(vinyl formate) must play an important role in steric control. This, however, did not appear to be the case with poly(vinyl acetate).

Rosen and co-workers (*23*) also showed that poly(vinyl formate) formed at low temperatures is syndiotactic. This, of course, is the preferred configuration in the free-radical-propagating species, requiring the least amount of activation

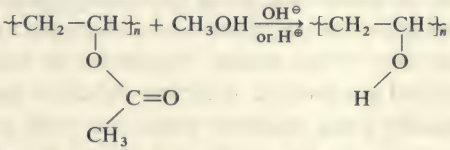
energy. At the same time, poly(vinyl acetate) prepared even at −35°C, still remained free of steric regularity.

Poly(vinyl acetate) has been copolymerized with a considerable number of other monomers. Among these, the more prominent ones are copolymers with vinyl chloride and with ethylene.

Although the r values are not favorable for copolymerizations with the acrylic and methacrylic monomers, many copolymers were prepared by a variety of processes. Emulsion systems appear particularly useful for such reactions (*24*, *25*).

12-10. Poly(vinyl alcohol)

As mentioned above, the product of hydrolysis from poly(vinyl esters) is poly(vinyl alcohol). Actually, the reaction is more conveniently carried out by means of an ester interchange. The polymer is heated in the presence of either ethyl or methyl alcohols catalyzed by acids or basis,



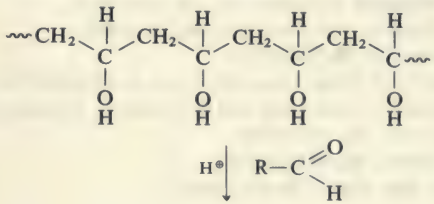
When the reaction is conducted with the aid of acidic catalysts, it tends to proceed at a slower rate than when it is catalyzed by bases. Also, in the presence of bases, some ether links tend to form.

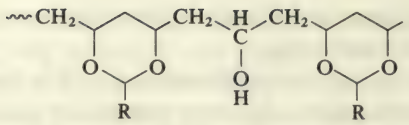
The polymer, although usually atactic, is highly crystalline (*26*, *27*). This crystallinity can be ascribed to the fact that the hydroxyl groups are too small to disrupt crystal lattices. Hydroxyl groups also form hydrogen bonds with adjacent groups to a high degree, which further aids crystallinity. By comparison the parent acetate groups are too bulky to fit into crystal lattices, so poly(vinyl acetate) is amorphous.

Poly(vinyl alcohol) loses water at temperatures of about 100°C, with the resultant formation of unsaturated links. The polymer is water-soluble, but aqueous solutions are unstable in the presence of acids and bases.

12-11. Poly(vinyl acetals)

Poly(vinyl alcohols) will undergo acetal condensation with aldehydes when acid-catalyzed. The reactions can be represented as follows:





Typical among these are poly(vinyl butyral) and poly(vinyl formal). It was demonstrated that approximately 13.5% of the hydroxyl groups remain unreacted in this reaction (*28*), because some hydroxyl groups become isolated.

12-12. Poly(vinyl ethers)

The most common methods of monomer syntheses consist of condensations of acetylene with alcohols in the presence of caustic (*29*),

$$ROH + CH{\equiv}CH \xrightarrow[130\text{–}180^\circ C]{KOR} CH_2{=}CHOR$$

Potassium hydroxide or alcoholate is the preferred catalyst, with the reaction usually being carried out in an autoclave under nitrogen atmosphere.

Polymerization of vinyl ethers cannot be carried to high-molecular-weight products via free-radical mechanism. Cationic initiation must be used instead. Lewis acids are typically good catalysts which will yield elastomers and solid polymers when the reactions are conducted at low temperatures. Poly(vinyl methyl ether) is soluble in water and a number of organic solvents.

Mixtures of vinyl ethers can be copolymerized by cationic mechanism to yield syrupy copolymers when reactions are conducted between 0 and 100°C. At lower temperatures solid polymers can be formed.

Copolymers of methyl, ethyl, and butyl vinyl ethers were reported (*30*) with vinyl chloride, acrylonitrile, dibutyl maleate, acrylic and methacrylic esters, and vinyl ketones. The reaction was conducted by free-radical mechanism using an emulsion-polymerization technique with persulfate initiation.

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Part IV

CONDENSATION POLYMERS

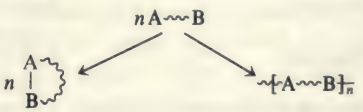
Mechanism of Polycondensation Reactions 13

13-1. Mechanism of Reaction

The addition polymerization reactions are all rapid. Each macromolecule is formed in 10^{-2}–10^{-5} seconds. This, however, is not true of condensation polymerizations. The syntheses of the macromolecules through condensations are accomplished in a series of individual steps which occur over a finite period of time. Overall reaction time is often measured in hours or even days. Furthermore, the molecular weights that are achieved by condensation polymerizations are often much lower.

Another important point about condensation polymerizations is the fact that only linear polymers result from bifunctional reactants, and branched structures are formed only via the incorporation of tri- and higher functional reactants. There are some situations, however, in which side reactions are possible which will effectively raise the functionality of some units above two, thereby leading to branching.

In general, bimolecular condensations can potentially lead to either inter- or intramolecular reactions, and the intramolecular condensations will lead to ring formations,



The path that the reactions will take is governed by the size of the ring. If intramolecular condensation will lead to strained rings, then the intermolecular condensations will be favored, but if they lead to strain-free rings, then intramolecular condensations would be favored. So if the resultant rings which can form will be less than five atoms or more then seven atoms in size, there appears little tendency for such ring formations, with the products usually consisting almost entirely of open-chain polymers. In the cases of six or seven atoms, on

the other hand, either rings or chains or both may form. Furthermore, a transformation is possible from rings to chain structures and back. As a matter of fact, advantage is taken of this in the formation of many polymers, such as, for instance, in the ring-opening polymerizations, although whether such cases are stepwise condensation reactions or ionic addition polymerizations is something that can be debated. In 1944 Flory tabulated (*1*) the types of six- and seven-membered molecules which tend to either polymerize into chains or form rings. These are shown in Table 13-1.

The facility with which such reversible transformations between the rings and chains can occur with various six-membered units is very interesting. For instance, six-membered cyclic esters polymerize spontaneously at moderate temperatures. Carothers et al. (*2*) have drawn attention to the parallelism between the ease of reversible polymerization of six-membered rings and their susceptibility to hydrolysis.

A good example of a typical condensation polymerization is the self-condensation of a hydroxy acid to form a polyester. The first step is intermolecular esterification between two monomers with the production of a dimer,

$$\text{HORCOOH} + \text{HORCOOH} \rightarrow \text{HORCOORCOOH} + \text{H}_2\text{O}$$

TABLE 13-1

Ring Formation vs. Chain Polymerization from Six- and Seven-Membered Units[a]

Type	Products of bifunctional condensation	
	6-membered unit	7-membered unit
ω-Hydroxy acid; self-ester	Both ring and polymer spontaneously interconvertible	Chiefly ring; interconvertible
α-Hydroxy acid; self-ester	Linear polymer is probably the primary product; Interconversion is easy	
Alkylene carbonate	Both ring and polymer easily interconvertible	Linear polymer only
Dibasic acid anhydride	Ring only	Linear polymer; convertible to ring
Alkylene formal	Ring only	Both ring and polymer interconvertible
ω-Amino acid; self-amide	Ring only	Both ring and polymer interconvertible at high temperatures
α-Amino acid; self-amide	Ring usually predominates, but some linear polymer can be formed; interconversion is difficult	
Alkylene sulfide	Linear polymer; converted with some difficulty to ring	
Alkylene ether–sulfide	Linear polymer	

[a] From Reference *1*.

This step may be followed by reaction of the dimer with another dimer to form a tetramer, and so on. The same species in turn may react with monomers dimers, and so on. All the reactions can be summarized by writing

$$x\text{-mer} + y\text{-mer} \rightarrow (x + y)\text{-mer}$$

in which $x + y$ assume every possible combination of positive integral values to be considered. In condensation polymerizations, in other words, there are no inactive polymer chains and the reactions between two polymer molecules occur as well.

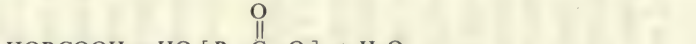
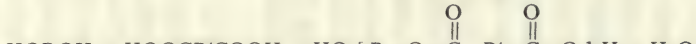
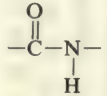
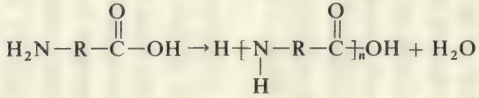
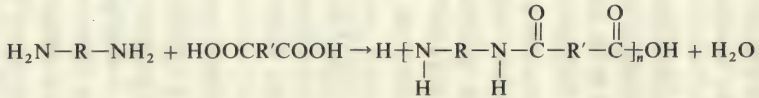
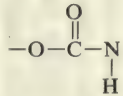
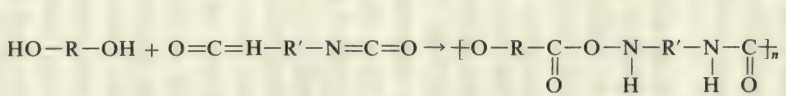
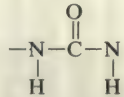
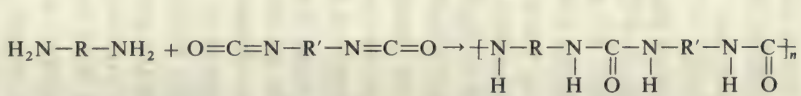
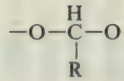
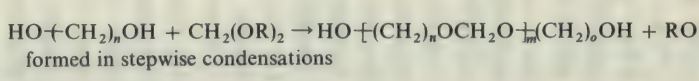
The various steps need not be belabored. All involve the same process, and Flory suggested (*3*) a basic assumption—that under suitable conditions the rate constant K may be assumed to be independent of chain length. The pertinent conditions are that (1) the distances separating the functional groups on each end of the difunctional molecule must be large enough so that they are essentially isolated from each other, and (2) the reaction is conducted under conditions of high concentration in solution or in the absence of solvents all together (in a melt), so that the process by which the functional groups come together for reaction involves only the motion of the heads or tails of the reacting molecules. Thus the entire polymerization process is regarded as a reaction between functional groups. The individual molecular species and the manifold steps in which they are involved are disregarded. Flory's assumption (*3*) may be an oversimplification; nevertheless, it is a useful assumption for kinetic interpretation.

Interruption of a linear, or bifunctional, condensation at the early stages of the reaction will result in having a polymer of low average molecular weight. But, unless the average degree of polymerization is very low, less than about 10 units, the product will contain a negligible quantity of monomer units (less than 1 %). With the continuation of the reaction, however, the low-molecular-weight polymers undergo further condensations, thereby increasing the average molecular weight. The final molecular weight in such reactions will only be limited by the attainable degree of completion of the condensation, or by side reactions that might consume functional groups without producing interunit linkages. Such could be the case if some monofunctional molecules were present as an impurity. So, in condensation polymerizations, the monomer disappears almost completely during the initial phase of the process, but, to attain a relatively high-average molecular weight, it is necessary to carry out the reaction until it approaches closely to completion.

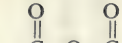
Just about all nucleophilic displacement reactions have found some application in condensation polymerizations. We list some of the more common ones in Table 13-2.

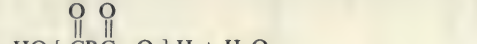
TABLE 13-2

Common Condensation Polymers

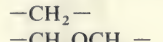
Type	Interunit linkage	Example
Polyester		
		
Polyamide		
		
Polyurethane		
Polyurea		
Polacetal		 formed in stepwise condensations

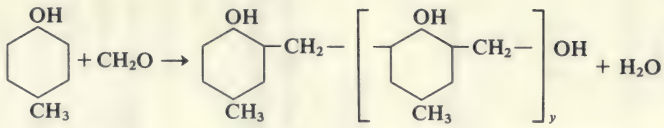
Polyanhydride



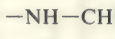


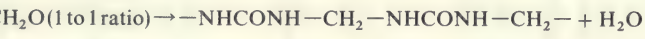
Phenol-aldehyde

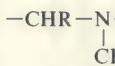




Urea-aldehyde

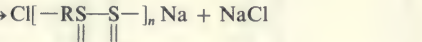






With excess CH_2O, three-dimensional network + H_2O

Polysulfide



13-2. Some Elementary Kinetics of Linear Condensation Polymerization

As an example, one can consider polyesterification reactions. Let C be the concentration at time t of free carboxyl or hydroxyl groups of all molecules present, and C_0 will then be the corresponding initial concentration before the start of polymerization. Then C_0/C is clearly the number average degree of polymerization, which can be called $\bar{X}_n$, since C molecules have C_0 monomer units incorporated within them. By introducing the parameter p, which represents the fraction of all functional groups that have reacted,

$$p = \frac{C_0 - C}{C}$$

we have, at any time t,

$$\bar{X}_n = \frac{C_0}{C} = \frac{1}{1 - p}$$

The rate of change of concentration C may then be written as the total rate at which the processes occur,

$$\frac{[-dC]}{[dt]} = K[\text{catalyst}]C^2 = K^1C^2$$

where $K' = K$ [catalyst]. Since the catalyst is not used up during the reaction, K' is a constant, independent of time. By integrating the equation we get

$$\frac{1}{C} = K't + \frac{1}{C_0}$$

This allows us to express $\bar{X}_n$ or p as a function of time:

$$\bar{X}_n = \frac{C_0}{C} = 1 + K'C_0t$$

$$p = \frac{K'C_0t}{1 + K'C_0t}$$

The fact that these equations are obeyed by reactions of this type was shown by Flory (*4*) in a study of the polymerization of decamethylene glycol and adipic acid in the presence of small amount of *p*-toluene sulfonic acid as catalyst (Figure 13-1).

There are no corresponding data for esterification of long-chain monofunctional acids and alcohols, so the assumption that the rate constant for such a reaction should be the same as the rate constant for polyesterification cannot be tested. The activation energy obtained by Flory (*4*) is $E = -Rd \ln K/d(1/T)$ = 11,200 calories. This figure is roughly the same as the activation energy of 10,000 calories observed for the esterification of aliphatic acids with methanol, catalyzed by HCl.

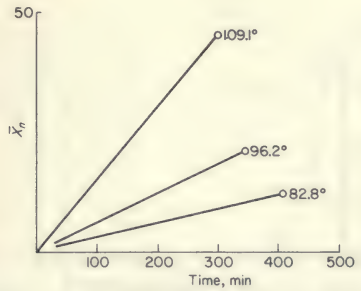


Figure 13-1. Reaction of decamethylene glycol with adipic acid catalyzed by *p*-toluene sulfonic acid. (From Reference *1*.)

If the condensation is carried out without a catalyst, then the equation becomes

$$\frac{[-dC]}{[dt]} = KC^3$$

and

$$(\bar{X}_n)^2 = \frac{C_0^2}{C^2} = 1 + 2KC_0^2t$$

One can define the extent of reaction p as the probability that a functional group has reacted at time t. So, then, the probability of finding an unrelated group at time t is $1 - p$.

If a given molecule at time t contains n units (mers), then it also contains $n - 1$ reacted functional groups (for it will possess one unreacted group on the end). As the probability of finding a single reactive group in a molecule at time t is p, then the probability of finding $n - 1$ of such reactive groups in the same molecule is p^{n-1}. Also, since the probability of finding the unreacted terminal group is $1 - p$, then the probability of finding an n-mer will be $p^{n-1}(1 - p)$.

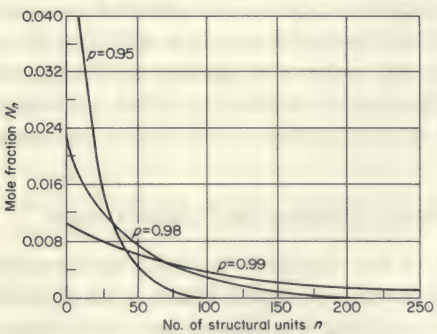


Figure 13-2. Relationship of N_n to n at different values of p. (From Reference *1*.)

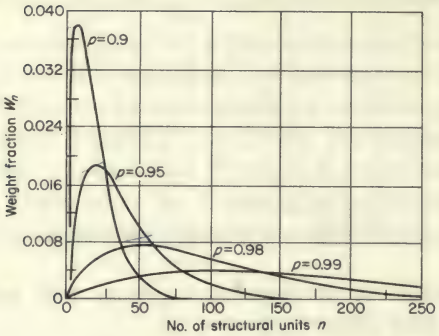


Figure 13-3. Relationship of W_n to n at different values of p. (From Reference *1*.)

This expression is also equal to the fraction of molecules which consists of n units. If there are N such molecules in total, the total number of N_n of n units is

$$N_n = Np^{n-1}(1 - p)$$

If the total number of mers present originally is N_0, then $N = N_0(1 - p)$ and $N_n = N_0(1 - p)^2p^{n-1}$ or the weight fraction W of n units can be written

$$W_n = \frac{nN_n}{N_0} = n(1 - p^2)p^{n-1}$$

Flory (*1*) illustrates these relationships in plots of N_n and W_n against n for different values of p (Figures 13-2 and 13-3).

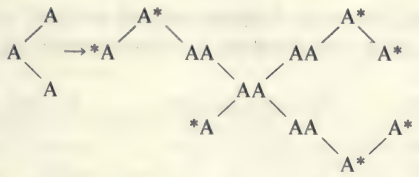
Generally speaking, on a number basis, there are more monomers present in the reaction medium than that of any other reaction species at all stages of the polymerization. But on a weight basis, the proportion of monomers and other low-molecular species (such as dimers and trimers) is very small, and this number decreases as the molecular weight increases.

To control the molecular weight of the product, one can actually stop the reaction when the desired molecular weight is achieved. If one does not do that, then the products are still subject to further molecular-weight changes with subsequent heating. This can be avoided by either adding a slight excess of one bifunctional reactant or a small amount of a monofunctional reagent.

13-3. Three-Dimensional Condensation Polymerization

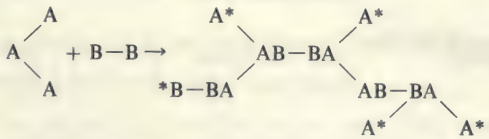
When one or both of the reactants has the functionality greater than two, three-dimensional condensations occur. Chain growth will not be restricted in one direction and the polymers produced are much more complex. We can illustrate such condensation by considering a trifunctional molecule that (*1*)

condenses with itself,



The unreacted groups (*) are capable of further growth. In addition, whereas branching is shown in two dimensions, it can obviously grow in three dimensions.

Outside of condensing with itself, the trifunctional molecule can also be visualized as condensing with another difunctional molecule,



The number of the potentially active groups (*) in both condensations increases per molecule as condensation proceeds and the size of the structures increases. At some stage of the condensation the networks become extremely large and *gelation* occurs. At this stage, the reaction mixture consists of two components; the *gel*, which is insoluble in solvents, and the *sol*, the part of the reaction mixture that is still soluble. The gel is actually composed of swollen three-dimensional networks and the sol of branched condensates.

13-4. Low-Temperature Polycondensations

Until now nucleophilic displacement reactions used for condensing low-molecular-weight species into macromolecules which are carried out at relatively high temperatures were discussed. Such reactions, in very many cases, are carried out in the melt without the aid of solvents. The melt preparation of a polyamide—for example, from a diacid and a diamine—requires not only high temperatures, but is usually first carried out under pressure, to prevent loss of the more volatile diamine, and then later under vacuum to achieve high molecular weights by shifting the equilibrium to the product side. Obviously such preparatory techniques are limited to thermally stable products.

Over the last 10 years, however, a new preparatory method, based on the Shotten–Bauman reaction, has evolved (*5–7*). It allows rapid preparation of condensation polymers at room temperature.

The process is possible because of the greater reactivity of an acid chloride with an amine than that of the free acid. So, when, say, a diacid chloride and a diamine are combined in the presence of an HCl scavenger, a rapid reaction

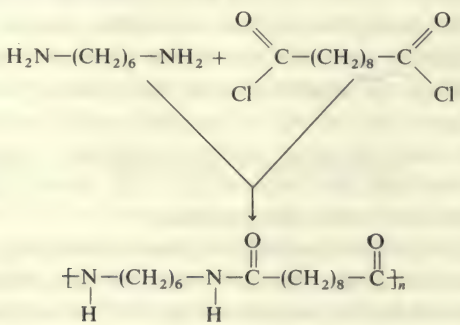
TABLE 13-3

Chemical Classes of Polymers which can be Formed from Low-Temperature Polycondensations[a]

Linking unit	Reaction conditions	Reacting groups
Amide	Two-phase system	$R-\underset{\displaystyle H}{\overset{\displaystyle |}{N}}-H + Cl-\overset{\displaystyle O}{\overset{\displaystyle \|\|}{C}}-R'$
Urea	Two-phase system	$R-\underset{\displaystyle H}{\overset{\displaystyle |}{N}}-H + Cl-\overset{\displaystyle O}{\overset{\displaystyle \|\|}{C}}-Cl$
	Two-phase system	$R-\underset{\displaystyle H}{\overset{\displaystyle |}{N}}-H + Cl-\overset{\displaystyle O}{\overset{\displaystyle \|\|}{C}}-\underset{\displaystyle R'}{\overset{\displaystyle |}{N}}-R'$
	Single-phase system	$R-\underset{\displaystyle H}{\overset{\displaystyle |}{N}}-H + O=C=N-R'$
Urethane	Two-phase system	$R-\underset{\displaystyle H}{\overset{\displaystyle |}{N}}-H + Cl-\overset{\displaystyle O}{\overset{\displaystyle \|\|}{C}}-O-R'$
	Single-phase system	$R-O-H + O=C=N-R'$
Ester	Two-phase system	$R-O-H + Cl-\overset{\displaystyle O}{\overset{\displaystyle \|\|}{C}}-R'$
Sulfonamide	Two-phase system	$R-\underset{\displaystyle H}{\overset{\displaystyle |}{N}}-H + Cl-\overset{\displaystyle O}{\overset{\displaystyle \|\|}{S}}-R'$ (O)
Phosphonamide	Two-phase or single	$R-\underset{\displaystyle H}{\overset{\displaystyle |}{N}}H + Cl-\overset{\displaystyle O}{\overset{\displaystyle \|\|}{P}}(R)(Cl)$
Carbonate	Single-phase system	$R-OH + Cl-\overset{\displaystyle O}{\overset{\displaystyle \|\|}{C}}-Cl$
Sulfonate	Two-phase or single	$R-OH + Cl-\overset{\displaystyle O}{\overset{\displaystyle \|\|}{S}}-R'$ (O)

[a] From Reference *8*.

takes place at room temperature,



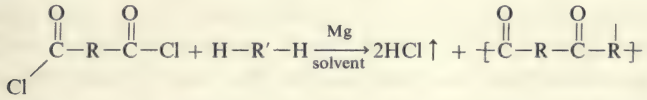
The average molecular size obtained by this method is equivalent to that obtained by the melt process.

The process is not limited to polyamides but is limited by reduction in reactivity of the intermediates. Table 13-3 shows some of the reactions possible by this procedure.

Most of these reactions are carried out by use of two immiscible liquid phases, one of which is usually water. The water phase would contain the diamine or the dialcohol and any added alkali. The other phase would consist of the diacid halide in an organic solvent such as tetrachloroethylene, chloroform, carbon tetrachloride, or xylene. The reaction occurs at or near the liquid interface, giving rise to the term *interfacial polycondensation.* Actually, though, few such reactions can be carried out in a single liquid phase, such as urethane formations (*9*) and that of polycarbonates (*10*).

13-5. Condensation Polymers by an Anhydrous Catalytic Solution Process

Matzner and co-workers (*11*) have reported the development of a new procedure for the preparation of condensation polymers, based on reacting a difunctional acid chloride or chloroformate in the presence of magnesium powder with a compound possessing active hydrogen atoms. The reaction is carried out in an invert solvent under reflux. It can be represented as follows:



This method was reported to be useful for the preparation of polycarbonates, polyurethanes, polyesters, polyamides, and polyureas. One unique advantage of this process is that it permits use of very weak bases, such as N,N′-diarylarylene diamines, which could not be previously incorporated into polyamides and polyurethanes by other means.

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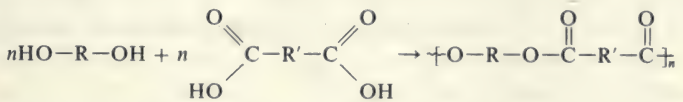
Polyesters 14

14-1. Linear Polyesters

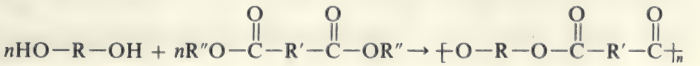
The polyesters comprise a large and important group of condensation polymers. Actually, this group of polymers has to be subdivided further into the linear polyesters, which give rise to many synthetic fibers and films and the branched polyesters of the coatings industry.

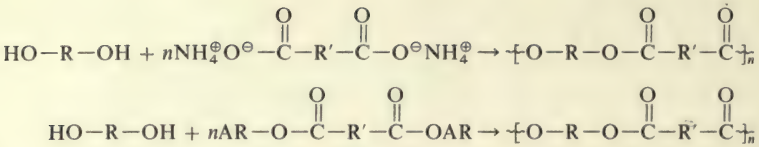
Carothers and Arvin (*1*) were the first to synthesize linear polyesters. These included condensation products from ethylene, trimethylene, hexamethylene, and decamethylene glycols with malonic, succinic, adipic, sebacic, and orthophthalic acids. This work later expanded (*2*) to include polyesters of oxalic acid and ethylene and poly(methylene glycols). Among these, the highest melting product was poly(ethylene oxalate), m.p. 172°C. Following these initial studies, many other polyesters were prepared by various investigators. Linear polyesters were the subject of one recent review article by Wilfong (*3*), in which eleven distinct synthetic methods were listed:

1. Stochiometrically balanced reactions are carried out between dibasic acids and glycols. Because failure to maintain strict stochiometry will prevent attainment of high molecular weights, the glycols are originally added in slight excess and then removed by vacuum or by sweeping an inert gas through the reaction mixture,

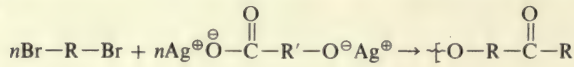


2. Through the reaction of a glycol with either an aliphatic ester, an amine salt, or an aryl ester of a dibasic acid,

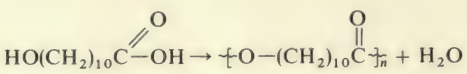




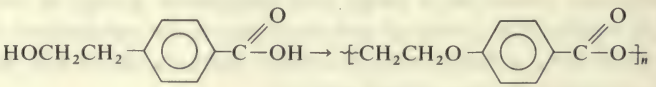
3. By reacting a silver salt of a dibasic acid and an aliphatic dibromide,



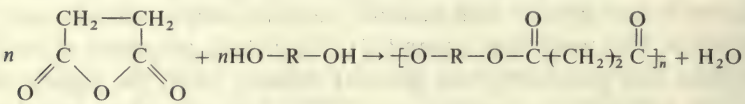
4. Through self-condensation on ω-hydroxy acid,



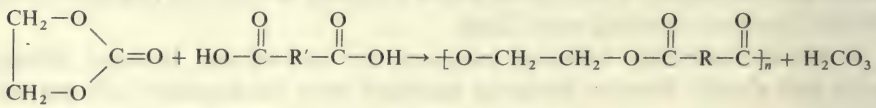
This method was used by Winfield (*4*) for the preparation of polyesters similar to poly(ethylene terephthalate),



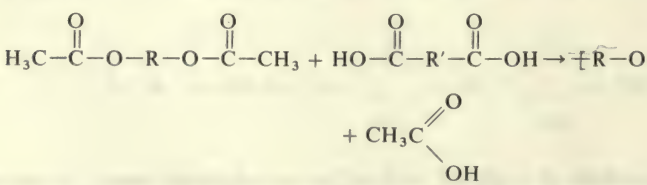
5. Through reaction of an acid anhydride and a glycol,



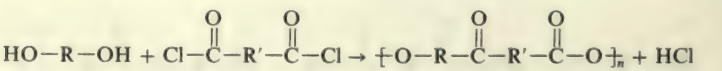
6. By transesterification of a glycol carbonate and a dibasic acid,



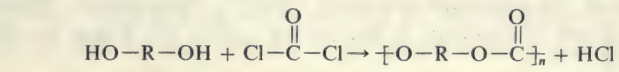
7. By transesterification of a glycol ester of acetic acid with a dibasic acid,



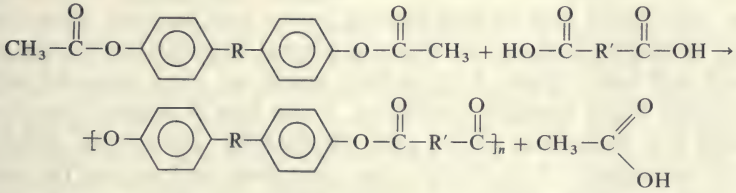
8. By reacting a diacid chloride with a glycol,



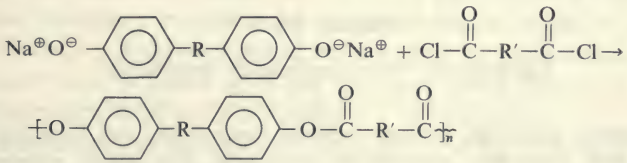
A special case of this condensation is the use of phosgene to form a carbonate,



9. Through reacting a diacetate of a diphenol with a dibasic acid,



10. Through reacting a diacid chloride with an alkali diphenate,



11. Through reacting a glycol and a dicarboxylic acid or its ester in an inert high-boiling liquid capable of dissolving appreciable amounts of product produced. The lower viscosity of the reaction medium promotes diffusion and removal of the moisture or the alcohol formed during the polyesterification.

One can summarize these methods with a generality by saying that just about all known methods of ester syntheses in organic chemistry were employed at one time or other to form polyesters.

Actually, though many methods have limitations and require care to be useful. Thus a direct reaction between a diacid and a dialcohol in the presence of a strong acid catalyst can often lead to only low-molecular-weight products, because of the difficulty of water removal. In addition, the high temperatures needed for the reactions may cause pyrolysis of the ester or even ether formation from the glycols if an improper catalyst were used.

Use of ester interchange is often very practical, as many free dicarboxylic acids (such as terephthalic) tend to be insoluble, and alcohol removal usually requires less energy than water. The limitation in using diacid chlorides and dialcohols lies in the higher cost of the acid chlorides.

Griehl and Schnock (*5*) observed that in ester interchange reactions the rate does not appear to be affected by the nature of the glycol used, although it is affected by the acid used. Thus the rate appears to be greatest with terephthalic acid and least with phthalic acid, with isophthalic acid occupying an intermediate position among the three. Benzoic acid esters exchange even less rapidly than phthalic esters do. Esters of sebasic acid appear to exchange almost as rapidly as the esters of terephthalic acid.

Much research has gone into various catalytic agents used in polyester formation. Some of the materials are more effective than others. Wilfong lists many different classes of catalysts in his review article (*3*). These are shown in Table 14-1.

The relationships between chemical structures of linear polyesters and their physical properties appear to be (*3*) as follows: High interchain forces and molecular inflexibility lead to high melting points and promote microcrystallinity. This, of course, is true of polymers in general. It is also known that in the case of very stiff bulky chains, high melting points are often observed without these polymers being actually crystalline. From this it follows that flexible chains with low interchain forces give low-melting, amorphous polyesters. So one can summarize (*3*) the factors that contribute to lowering the melting points: (1) structural irregularity, (2) angled chains arising from monomer units

TABLE 14-1

Catalysts for Polyesterification Reactions[a]

1. Lithium, sodium, potassium, calcium, beryllium, magnesium, zinc, cadmium, strontium, aluminum, lead, chromium, molybdenum, manganese, iron, cobalt, germanium, nickel, copper, silver, mercury, tin, platinum, boron, antimony, bismuth, palladium, and cerium as the metal, oxide, hydride, formate, acetate, alcoholate, or glycolate
2. Zinc and lead perborates and borates
3. Zinc, manganous, cobalt, magnesium, and cadmium succinate, butyrate, adipate, etc., or enolate of a diketone
4. Calcium, zinc, aluminum, and strontium chlorides and bromides
5. Lanthanum dioxide and titanate
6. Neodymium chloride
7. Double salts of antimony, such as potassium antimonyl tartrate, and salts of antimony acids, such as potassium pyroantimonate
8. Diethyl sulfate
9. Lithium, zinc, or manganese salts of dithiocarbamic acids
10. Cobalt naphthanate
11. Titanium tetrafluoride or tetrachloride
12. Alkyl orthotitanates
13. Titanium tetrachloride—ether complexes
14. Quaternary ammonium salts containing a titanium hexalkoxy radical; titanium tetralkoxides; alkali or alkaline earth metal compounds with aluminum, zirconium, or titanium alkoxides
15. Tertiary amines
16. Organic silicates
17. Magnesium metal plus free iodine
18. Organic quaternary ammonium, sulfonium, phosphonium, and oxonium hydroxides and salts
19. Calcium, strontium, or barium malonate, adipate, benzoate, etc.
20. Lead, zinc, cadmium, or manganese salt of the monoalkyl ester of a phenylene dicarboxylic acid
21. Antimonyl catechol complexes with an amine alcohol or an amine and an alcohol
22. Uranium trioxide, tetrahalide, nitrate, sulfate, acetate, etc.

[a] From Reference *3*; courtesy *Journal of Polymer Science.*

composed of odd numbers of atoms, (3) flexible bonds between the chains, (4) interchain attraction caused primarily by various dispersion forces, and (5) bulkiness of side groups. On the other hand, factors that contribute to high melting points are (1) presence of secondary bond forces, (2) stiffness of the internal bonds, (3) symmetry of the structure of the molecules, and (4) ability of the linear chains to pack closely.

Use of copolymerization to disrupt regularity is a well-established method. Flory (*6*) pointed out that when a polymer is modified through copolymerization, the product will have a depressed melting point in direct proportion to the molar fraction of the modifying agent. Coleman (*7*) has demonstrated that this relationship can be used to cause substantial modifications of polyesters without significantly lowering their melting point by picking modifying agents of very high molecular weight. Izard (*8*) bases his explanation of the copolymer effect on the fact that with the increase in size of the substituent group, the melting point passes through a minimum for any homologous series for condensation polymers. Bunn (*9*), on the other hand, believes that the minimum in the polyester melting-point curve is based upon the increased chain flexibility which comes from the introduction of easily rotatable C—O—C bonds.

Spatial isomerization also leads to irregularity of structure and the lowering of the melting point. Thus Wilfong (*3*) points to the fact that a *cis-trans* mixture poly(ethylene hexahydroterephthalate) is amorphous, whereas poly(ethylene-*trans*-hexahydroterephthalate) is crystalline with $T_m = 120°C$.

Doak and Campbell (*10*) reported that poly(decamethylene *d*-tartarate) has a crystalline melting point of 66°C, whereas the *meso* isomer melts at 33°C.

Carpenter (*11*) reported that monomers made up of even-numbered atoms yielded polymers which were straight chain and had a high melting point. On the other hand, those composed of odd numbers of atoms had lower melting points, owing to inclined valence angles causing helical coiling of molecules, thereby interfering with interchain cohesion.

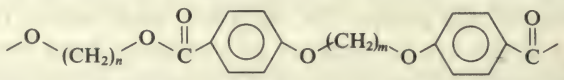
Variations in melting points with structure are shown in Table 14-2. Resonance and strong interchain polarization forces lead to high melting points and microcrystallinity. Destroying ring resonance by hydrogenation then results in a major drop in the melting points. This, again, is true of polyesters as well as of other macromolecules. The melting points of a number of representative polyesters are presented in Table 14-3.

Substitution of methylene groups in polyesters (and again this is true of other polymers as well) with oxygen atoms tends to increase free rotation, which results in lowering the melting points, particularly among aliphatic chains. At the same time, the oxygen atoms, because of their polarity, will tend to increase the cohesive attractive forces, thereby creating a stiffening effect and raising the melting point, particularly among aromatic groups.

Table 14-4 demonstrates the effect of ether linkages on melting points. Table 14-5 shows the effects of the number of methylene groups in aliphatic diacids on the melting point of the resultant polyester.

TABLE 14-2

Variations in Melting Points with Structures of Linear Polyesters[a]

Repeating unit: 

Values of n, when $m = 2$	m.p., °C	Values of m, when $n = 2$	m.p., °C
2	240	2	240
3	190	3	160
4	180–215	4	180
5	150	5	100
6	170–175	6	175
10	135		
18	119–122		

[a] From Reference *3* and other sources in the literature.

TABLE 14-3

Relationship of Structure to Melting Point of Linear Polyesters[a]

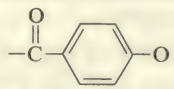
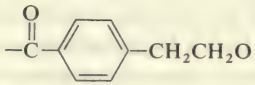
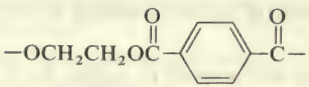
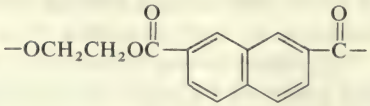
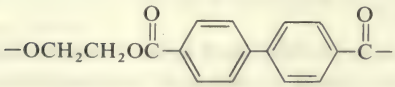
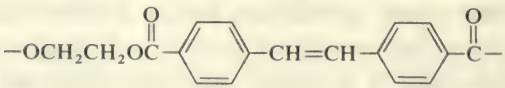
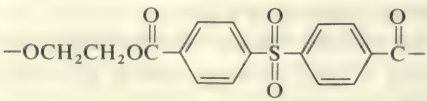
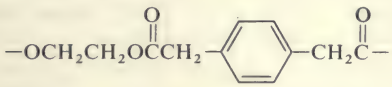
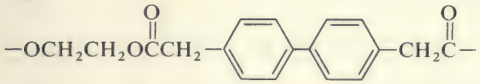
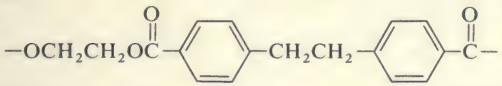
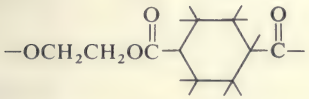
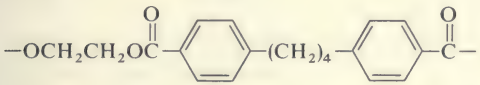
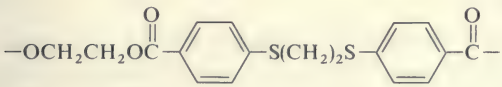
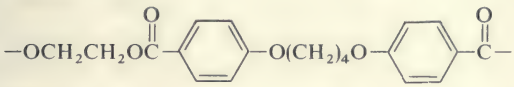
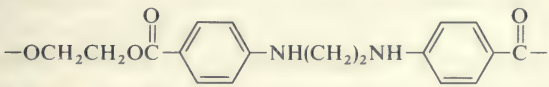
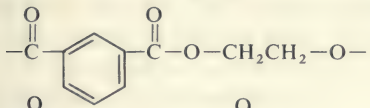
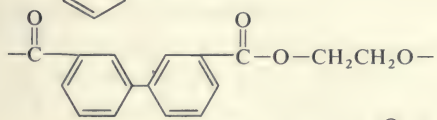
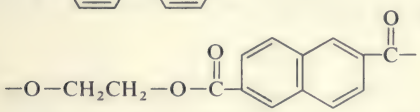
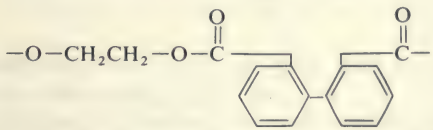
	Structure of monomer unit	T_g, °C	m.p., °C
1.		—	320
2.		—	185
3.		69	264–284
4.		119	270
5.		—	355
6.		—	420
7.		—	380

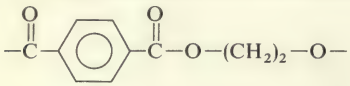
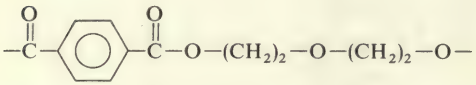
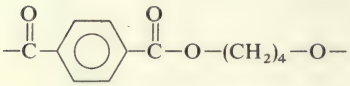
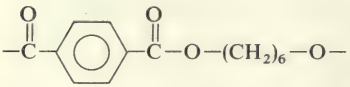
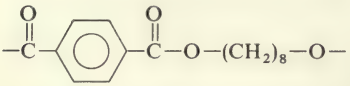
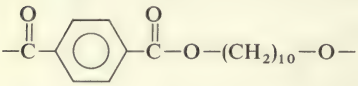
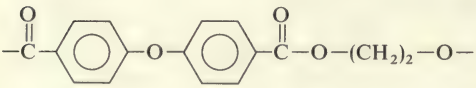
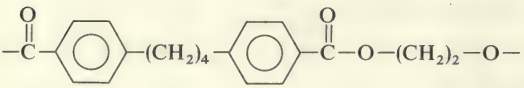
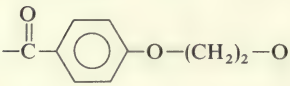
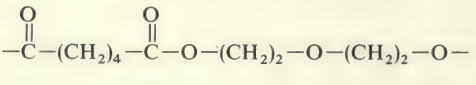
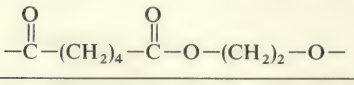
TABLE 14-3 *(continued)*

	Structure of monomer unit	T_g, °C	m.p., °C
8.		—	137
9.		—	150
10.		—	220
11.		—	120 (*trans*) <30 (*cis*)
12.		—	170
13.		—	200
14.		—	252
15.		—	273
16.		51	143, 240
17.		—	156
18.		113	260
19.		—	132

[a] From Reference *3* and other sources in the literature.

TABLE 14-4

Effect of Ether Linkages on Melting Points of Polyesters[a]

Structure of repeating units	T_g, °C	Approx. m.p., °C
	—	265
	—	Low
	<80	226–232
	—	145–152
	<45	129–132
	<25	129–138
	—	152
	—	170
	—	203–220
	—	<0
	−50, −30	48

[a] From various sources in the literature.

TABLE 14-5

Effect of Number of Methylene Groups in Acids on Melting Points of Polyesters[a]

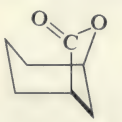
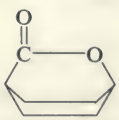
	Glycol, approx. m.p., °C			
$HO-\overset{O}{\overset{\|}{C}}-(CH_2)_n-\overset{O}{\overset{\|}{C}}-OH$	$-O(CH_2)_2O-$	$-O(CH_2)_3O-$	$-O(CH_2)_6O-$	$-O(CH_2)_{10}O-$
$n =$				
0	172	89	—	80
1	—	—	—	40
2	108	52	—	68–70
3	—	—	56	61
4	50	46	—	77
5	—	—	—	70
6	—	52	57	79
7	—	—	—	—
8	72–79	58	67	74–79
9	—	—	—	—
10	—	76	—	—

[a]From Reference *3* and other sources.

No discussion on the synthesis of polyesters would be complete without mentioning polyester formation by ring-opening reactions. These polymerizations by chain mechanism readily yield polymers from cyclic esters of three-, four-, seven-, or eight-membered rings (*12*). The five-membered lactones fail to polymerize, but the six-membered lactones can be converted to their corresponding polymers, provided they are not substituted by such bulky groups as *n*-propyl or are distributed by two methyl groups.

A number of bases are capable of catalyzing ring-opening polymerization of lactones. Such are: Na, NaH, K_2CO_3, CaH_2, H_2O, and $Ti(i\text{-}C_3H_7O)_4$. Sulfonic acid is also capable of ring-opening polymerization of lactones. Polymers from lactones, however, show a tendency to depolymerize and revert to the monomer. This detracts from their usefulness.

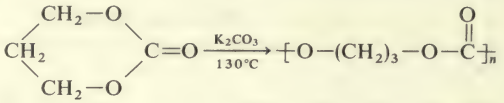
Hall (*13*) observed a number of six-membered bicyclic lactones that will, because of internal strain, yield mixtures of polymers and monomers when subjected to polymerization conditions. Such are


and


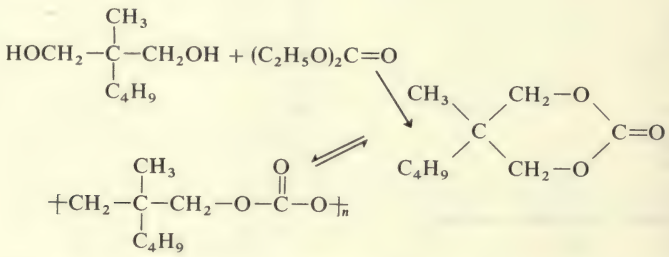
Propiolactone and butyrolactone will polymerize quite rapidly but yield relatively low melting polyesters.

In addition, Carothers demonstrated (*14*) that some cyclic carbonates, oxalates, and glycolates can be polymerized by ring-opening polymerization.

Thus the trimethylene carbonate will polymerize to yield a polymer with molecular weight of approximately 4000,

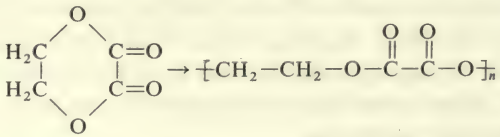


Sorel and Pohoryles (*15*) reported that among the various disubstituted cyclic carbonates, when one substituent is a methyl group and the other an *n*-propyl or isoamyl group, polymers are formed directly from the glycol and diethyl carbonate,

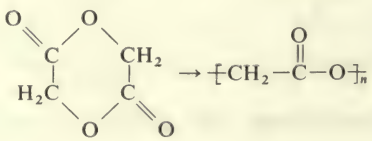


If however, the substituents are both ethyl groups, or hydrogens, or one an ethyl group and the other a phenyl group, or when higher glycols are used, such as 1,3-butanediol and 2,4-pentanediol, cyclic carbonates are formed that can then be converted to the corresponding polymers.

Carothers also noted (*14*) that ethylene oxalate will polymerize on standing to form a relatively low molecular weight product,

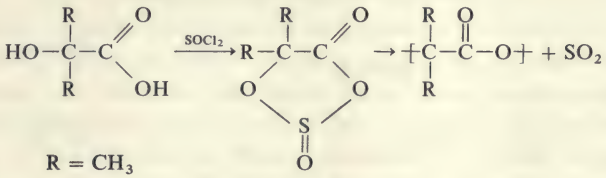


Lowe found (*16*) that although polymerization attempts on hydroxyacetic acid only lead to a lactide, Lewis acid can cause the lactide to form a high-molecular-weight material,



Bawn and Ledwith (*17*) reported an interesting synthesis of polyesters from α-hydroxy carboxylic acid by forming anhydrosulfites, which can then be

polymerized thermally with the loss of sulfur dioxide,

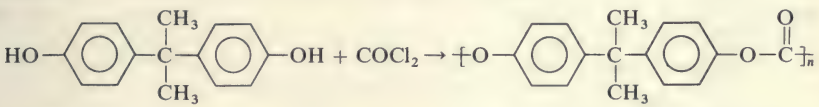


The polymer melts at 240°C and has a molecular weight of 100,000.

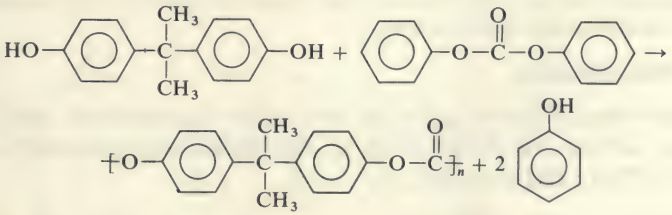
14-2. Polycarbonates

Polycarbonates are special types of polyesters, some of which possess high impact and tensile strength. Among these the most useful to date is the reaction product of phosgene and 2,2′-bis(4-hydroxyphenyl) propane (*18–22*). It can also be prepared by an ester interchange of diphenyl carbonate and the diphenol.

The reaction with phosgene is usually carried out at room temperature in a Lewis-base-like pyridine or in a two-phase system consisting of methylene chloride–aqueous sodium hydroxide,



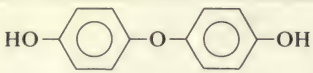
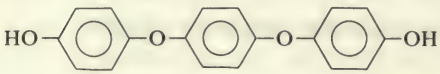
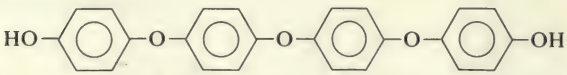
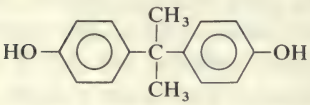
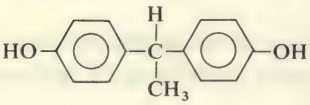
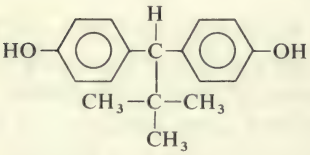
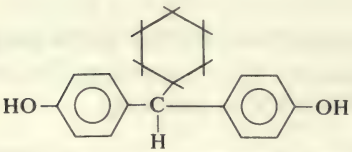
The ester-interchange reaction is carried out at 200–230°C at 20–30 mm Hg in a solventless system. This leads to approximately 90% conversion. The reaction is then completed at a temperature of 290–300°C at 1 mm Hg.



The product, sold in this country under the trade name Lexan, has a T_m of 270°C and T_g of 145–150°C. The polymer shows 20–40% crystallinity and appears to have a very high molecular weight.

Whereas the polycarbonate of 2,2′-bis(4-hydroxyphenyl) propane has achieved commercial importance, a number of other polycarbonate esters are known. Their T_m's and T_g's are shown in Table 14-6.

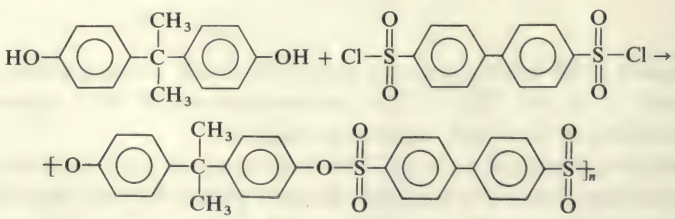
TABLE 14-6
Melting Points of Polycarbonates[a]

Structure of diphenol	Approx. T_m, °C	Approx. T_g, °C
	180–190	—
	205–210	—
	250–260	—
	265–270	145–150
	185–200	125–130
	170–180	145–150
	240–250	170

[a] From various sources in the literature.

14-3. Polysulfonates

Another special type of polyester now achieving industrial significance is an aromatic sulfone. Its preparation by interfacial polycondensation was described by Conix and Laridon (*23*),



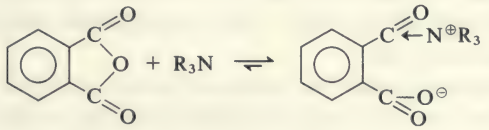
The crystalline polymer melts at 165°C.

14-4. Polyesters from Epoxides and Anhydrides

Fischer (*24*) reported a novel method of linear polyester formation by reacting an anhydride and an epoxide in the presence of a tertiary amine. In the presence of such bases, the two reactants appear to become bifunctional toward each other, so that their interaction yields linear macromolecules. The reaction appears general for terminal epoxides. Potentially this method permits the formation of linear polyester chains containing at regular intervals along the chain various substituents that could be used for further reactions. The reaction appears to proceed cleanly at 70–100°C and, when stochiometry is maintained, the residual acidity is low.

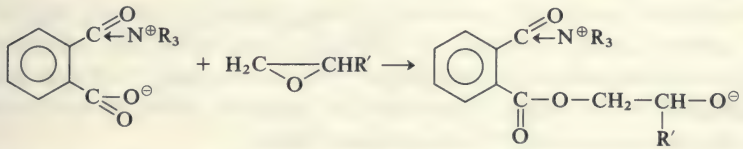
The mechanism can be represented as follows:

1. Activation of anhydride by the amine,



Owing to a large excess of the anhydride over the amine, the equilibrium is shifted to the right.

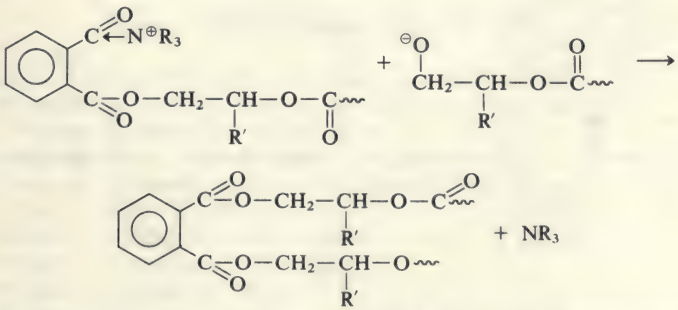
2. Reaction of the carboxyl anion with the epoxide,



3. The alkoxide anion then reacts with the anhydride,

The continuation of these steps should give rise to a polyester.

4. A displacement of the amine by alkoxide ion would also lead to polyester formation,



The method leads to polyesters that range in molecular weight from 6000 to 27,000, depending on the purity of the starting materials.

14-5. Alkyds

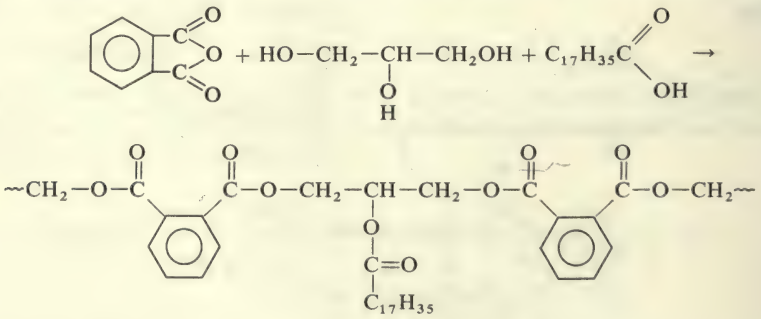
The alkyds are a special family of three-dimensional polyester resins used by the coatings industry (*25*, *26*). These polyesters are condensation products from dibasic acids or their anhydrides and trifunctional or tetrafunctional alcohols. The most common acid used for such preparations is phthalic acid (actually it is anhydride); the most common polyalcohol is glycerol (when tetrafunctional polyalcohol is needed, it may be pentaerythrilol). Such resinous condensation products of phthalic anhydride and glycerin are also often referred to as *glyptal resins.*

The alkyds are converted in their final form into three-dimensional or cross-linked products. In their soluble form, however, they are often essentially linear (with perhaps some branching). Usually a monofunctional vegetable oil fatty acid is included in the preparation to act as a modifier, by virtue of the esterification of the surplus hydroxyl groups of the polyalcohols, thereby also making the alkyd resin a synthetic oil.

The alkyd raw materials may be introduced as such or combined with some other material. Thus fatty acids may be added directly to the alkyd reactor, or they may be added, combined with glycerol, as an oil molecule. The higher-grade materials are usually prepared from free fatty acids, as they allow the chemist greater latitude in attaining the desired reaction products. The sequence of addition of the polymer ingredients is believed to be important in building up desirable structures.

In the preparation of these polyesters from glycerides, the first stage of the reaction almost always consists of forming a monoglyceride structure by alcoholysis of the oil with the added polyol. This is a necessary first step, because the transesterification reaction converts the insoluble polyhydroxy molecule and the oil phase into a single homogeneous phase.

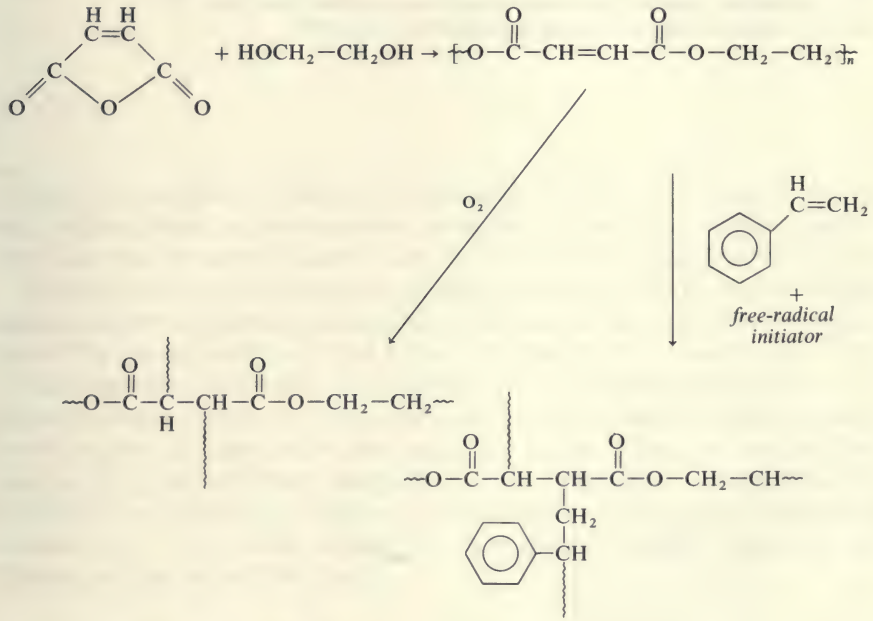
The progress of polyester formation is usually followed and controlled by periodically spot-checking the acidity and viscosity of the alkyd. If free fatty acids are used, the reaction can be illustrated as follows:



If the monofunctional acid is fully saturated, the alkyd is referred to as a *nondrying* one, by virtue of the fact that its film will not pick up oxygen and then

cross-link through an oxydation mechanism. If, however, it is unsaturated, the alkyd is capable of the reactions of the drying oils and can then build complicated, cross-linked molecules.

Sometimes the alkyds are deliberately made to be linear polyesters in which a dialcohol and dibasic acids are used. Here, however, part of the phthalic anhydride might be replaced by an unsaturated diacid or an anhydride (such as maleic anhydride). The resultant polyester then contains residual unsaturation in the backbone. Such a polyester can be cross-linked by addition of olefinic monomers and free-radical initiators to cause three-dimensional polymerization,



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15 Polyamides

There are two general groups of polyamides: synthetic and naturally occurring. In this chapter we shall concern ourselves only with the synthetic species. These also bear the generic name nylons, an adaptation through common usage.

The family of synthetic polyamides is large. As a result, also through common usage, a numbering system was adopted to distinguish the nylons by a designation of the starting material. Thus nylon 6 designates that it is a product from a single monomer composed of six carbon atoms, ω-aminocaproic acid, or a polycaproamide. Nylon 11 was prepared from a monomer possessing eleven carbon atoms, 11-aminoundecanoic acid, and so on. When two numbers are used, as in nylon 6-10, they designate that the polyamide is a condensation product of two species (although not a copolymer)—in this case, a six-carbon diamine and a ten-carbon diacid. The first number usually represents the diamine and the second the diacid.

15-1. Syntheses of Polyamides

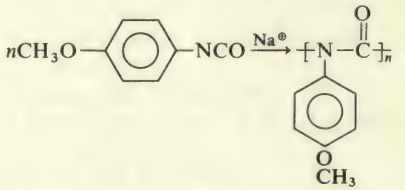
The syntheses of nylons are quite diverse. A separation will, therefore, be made here for convenience purposes, based on the type of polyamide under discussion, or on the method of synthesis, wherever such generalizations are possible.

Nylon 1

Substituted nylon 1 can be prepared by the method of Shashoua (*1*), who reported that isocyanates will polymerize by anionic mechanisms. Sodium cyanide is a useful catalyst and the reaction is conveniently carried out at -20 to $-100°C$,

$$n\mathrm{RN{=}C{=}O} \xrightarrow{\mathrm{Na}^{\oplus}} \left[\mathrm{N}(\mathrm{R})-\mathrm{C}(=\mathrm{O})\right]_n$$

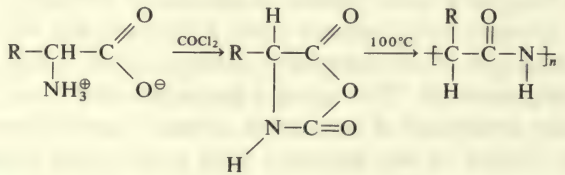
where R = CH_3; C_2H_5; C_4H_9; Ar; etc. As an interesting example of this reaction one can cite polymerization of *p*-methoxyphenylisocyanate (*1*),



These polymers can be formed in high molecular weights (approaching 1,000,000). When R is *n*-butyl or larger, these macromolecules are soluble in benzene, from which tough films can be cast. Nylon 1 polymers tend to depolymerize in the melt or in solution in the presence of catalysts.

Nylon 2

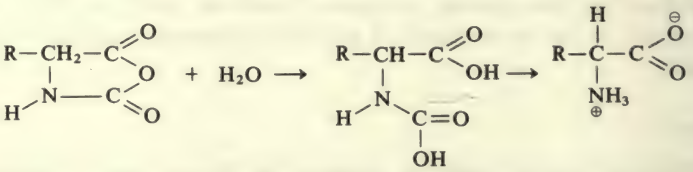
Lauchs (*2*) and Lauchs and Geiger (*3*) demonstrated many years ago that carbon anhydrides of α-amino acids will polymerize, with accompanying loss of CO_2,

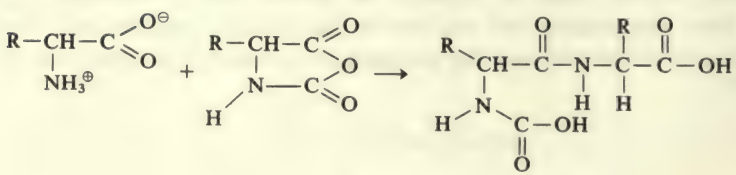


Here R can be either a proton or an alkyl group. Hanby and co-workers (*4*) reported the polymerization of glutamic acid by this route, obtaining polymers of molecular weight of about 21,000. Much higher molecule weight polymers have been attained since then by this reaction.

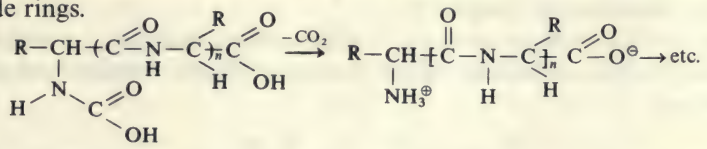
Woodward and Schramm (*5a*) suggested that the mechanism of polymerization might involve the hydrolysis of the anhydride to form an unstable *N*-carboxyamino acid which loses carbon dioxide to give the amino acid initiator:

Initiation:



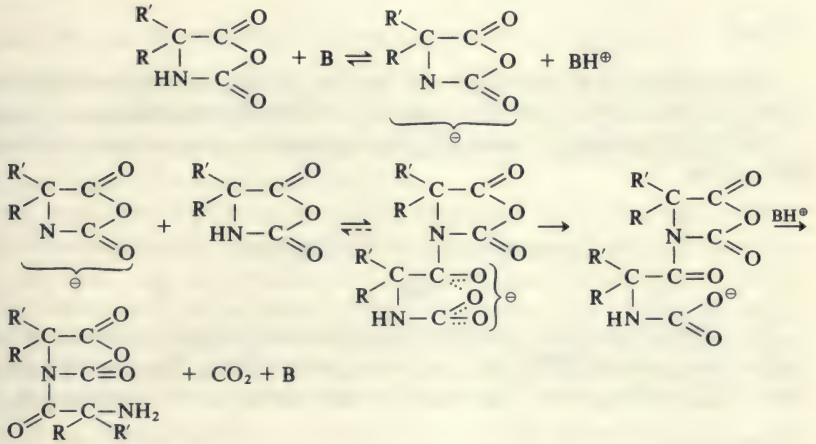


Propagation: successive losses of CO_2 are followed by successive openings of anhydride rings.

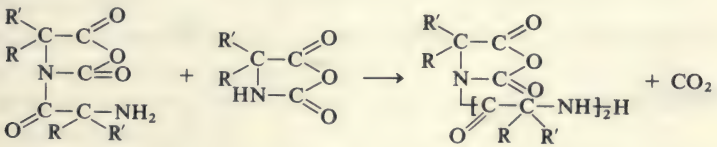


Ballard and Bambord, however, picture the mechanism to proceed as follows (*5b*):

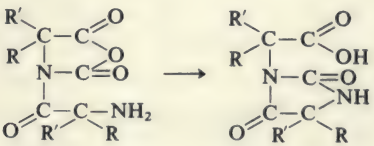
Initiation:



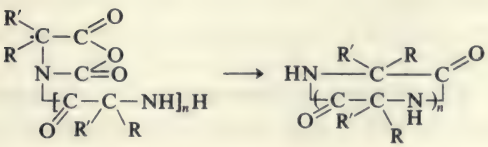
Propagation:



Termination:

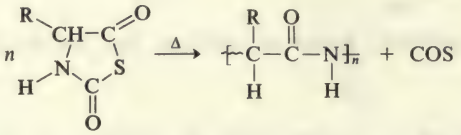


or



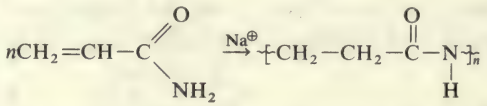
Nylon 2 synthesis has its greatest utility in research work on polypeptides. This will be discussed in Chapter 21.

An analogous reaction with *N*-carboxythioanhydrides is possible (*6*, *7*), also leading to high-molecular-weight products. Higher temperatures are required, however.



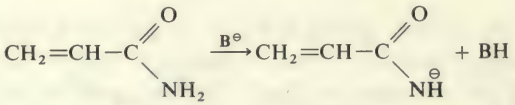
Nylon 3

Nylon 3 can be prepared by the method of hydrogen-transfer polymerization. This reaction is actually a case of a Michael-type addition of acrylamide to itself to form poly(*β*-alanine) (*8*). Such a reaction is an anionic addition polymerization,

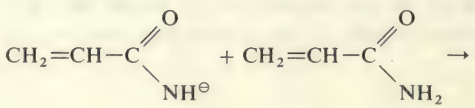


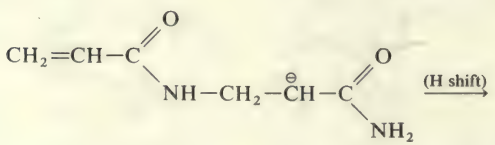
The polymerization is catalyzed by various bases, such as sodium alcoholates and sodium metal (100°C) in pyridine or acetonitrile. The resulting polyamide has a high melting point. The reaction mechanism can be explained as follows:

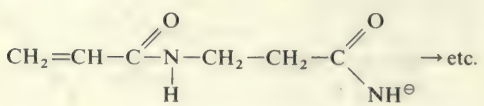
Initiation:



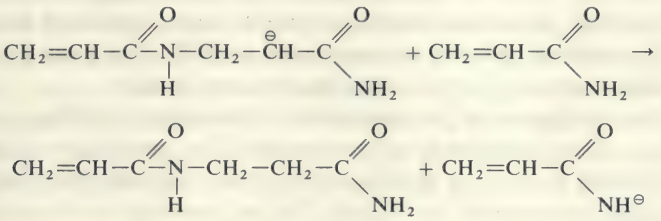
Propagation:







Termination can be by chain transferring to monomer from the intermediate,



Polyamides Obtained by Ring-Opening Polymerization of Lactams

A convenient route to the preparation of a number of polyamides lies in ring-opening polymerizations of the cyclic monomers. Hall (*9*) investigated the general effects of structure and catalysts on the polymerization of lactams. As a result, he was able to draw some conclusions:

1. Water and sodium hydride are equally effective catalysts above 200°C. At room temperature water is ineffective, whereas NaH is still a potent catalyst.
2. All the eight- and nine-membered ring compounds examined could be polymerized. Only half the seven-membered ring compounds studied, however, could be polymerized. Among the six-membered lactams only α-piperidine polymerized. 2-Pyrrolidine was the only five-membered lactam that Hall was able to polymerize.
3. Aryl or alkyl substituents on the ring decrease polymerizability, especially if the substitution is on the nitrogen atom.
4. The presence of other heteroatoms in lactam either reduces polymerizability or has no effect.
5. Thiolactams (iminethiones) are markedly less prone to polymerization than their corresponding oxygen analogs.

In a subsequent paper (*10*), Hall reported that cyclic ureas and thioureas failed to yield polymers at all.

All told, a great number of methods are known for the polymerizations of lactams (*11*). The monomer may actually be heated in an inert atmosphere without the aid of any catalysts for a period of 200 hours at 220–250°C to yield a polymer of high molecular weight. This procedure, however, can be reduced to 6 hours by the addition of small amounts of water or alcohol. Catalysts such as NaoH and KoH or Na_2CO_3 and K_2CO_3 were found to be effective (*10*, *11*). Alkali metals and their hydrides, such as sodium and lithium hydride (*10–12*), will also cause a rapid polymerization. Sulfonic acid (*10*) and dry hydrogen chloride (*13*) will effect polymerization at 245°C in a short time.

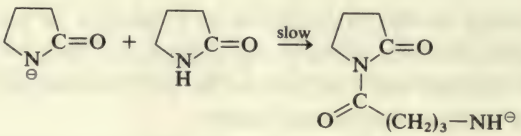
In addition to various catalysts, polymerization cocatalysts are also known. Such is N-acetylcaprolactam, which promotes anionically initiated polymerizations of ε-caprolactam (*14*). Thus, although metal- or metal-hydride-initiated polymerizations are normally conducted at higher temperatures and pressures,

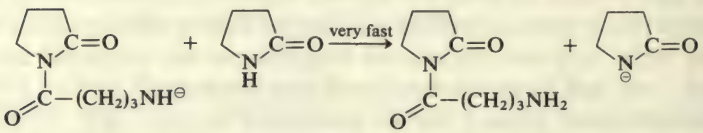
when N-acetylcaprolactam is present the reaction can proceed almost at room temperature (*15*), or at least 100° below the temperature required in its absence.

In addition, there are cocatalysts that promote water-catalyzed polymerizations (*16–21*), enabling them to be conducted at 180°C. Such are phosphonic and boric acids, sodium phosphite, and magnesium formate.

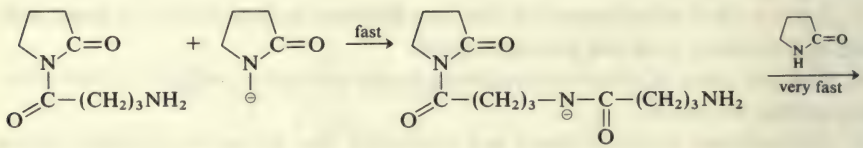
Whether the mechanism of polymerization is the same or different for water as well as for acid or for bases is not yet certain. Most investigators agree that a chain mechanism is involved in at least the anionically initiated reaction (*22*). This was originally postulated by Hall (*9*). The polymerization of pyrrolidine to yield nylon 4 was pictured by Hall as follows:

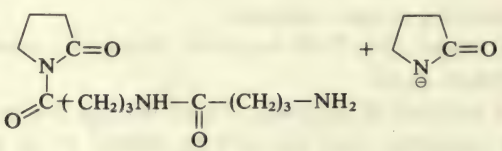
Initiation:





Propagation:



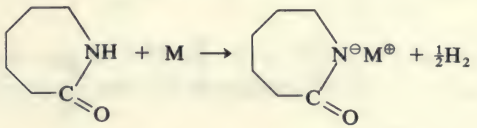


This mechanism is expected to apply to other lactams.

Ogata investigated (*23*) the effect of the resonance of the amide group on the polymerizability of lactams in the presence of water. He was able to conclude that the polymerizability of lactams in the presence of the same quantities of water were in the following order: eight-membered > seven-membered > eleven-membered ≫ five- and six-membered. In addition, the conformation of the amide group in six- to eight-membered lactams is *trans*, whereas in those with less than six members it is *cis*. The eight-membered lactams appears to have an equal number of *cis* and *trans* groups (as found from infrared spectra). This led Ogata to conclude that when the conformation of the two amide groups

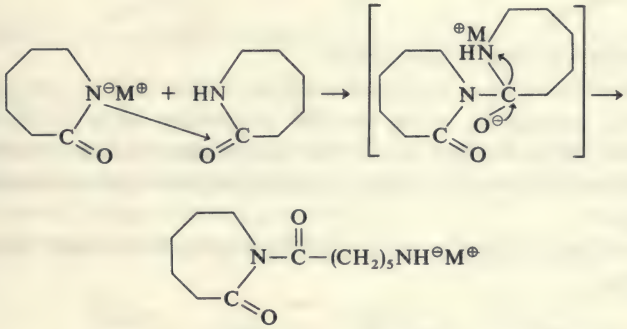
becomes equal, the resonance effect of the amide group decreases, resulting in an increase in the polymerizability of the lactam.

Yasumoto observed (*24,25*) that kitenimines and imino chlorides are useful cocatalysts for anionic polymerization of ω-lactams. They shorten the induction period, with the polymerization proceeding rapidly at low temperature, below the melting point of the polymer. Yasumoto (*25*) postulates that the reaction proceeded as follows. In a regular anionic polymerization the ε-caprolactam reacts with the alkali metal, yielding an iminium salt,



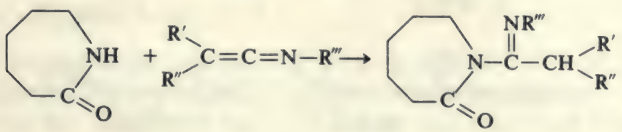
where M can be K, Na, and so on. Such a salt can also form through reaction with a Grignard reagent (*26*) or $LiAlH_4$.

The iminium salt then reacts with another molecule of caprolactam to form N-acyllactam (*27*),

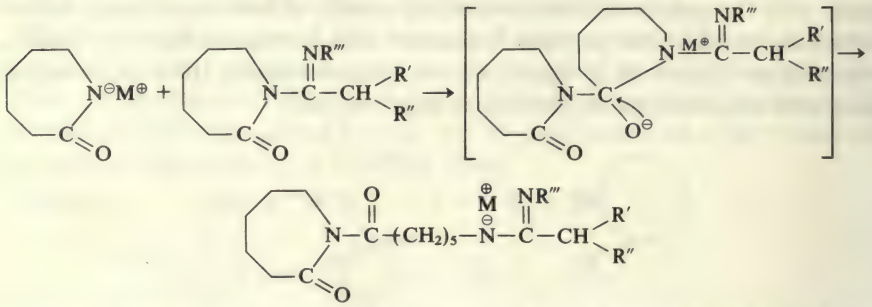


It is assumed that the group $-NH^{\ominus}M^{\oplus}$ shown above disappears and a new iminium salt of the lactam forms, not only because of the enormous prevalence of amide groups, but also because the $-NH^{\ominus}$ anion is a much stronger base than the amide of the lactam. The carboxyl group of the N-acyllactam is attacked by the lactam anion. This is followed by the opening of the N-acyllactam ring, and by the subsequent stepwise addition of anionic lactam, yielding the polymer (*24,25*).

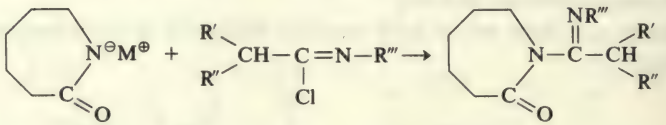
Based on the above, Yasumoto suggests (*24*) that the ketenimine reacts with a lactam to form an N-imidoyllactam as a reaction intermediate,



The lactam anion then attacks the N-imidoyllactam by the same mechanism as it does N-acyllactam, with the resultant opening of the ring of N-imidoyllactam. The propagation would then proceed continuously by stepwise addition of the anionic lactam,



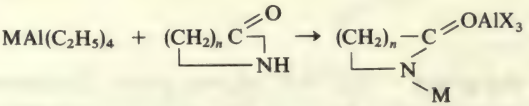
Yasumoto believes the imino chlorides also form N-imidoyllactams,



leading to polymerization, as previously.

Tani and Konomi (*28*) investigated polymerization of five-, six-, and seven-membered-ring lactams by using metallic potassium or a metal aluminum alkylate, $MAl(C_2H_5)_4$ as catalysts. In the latter case, the metal moieties were either potassium, lithium, or sodium. N-acyllactams or diphenyl ketene served as the cocatalysts.

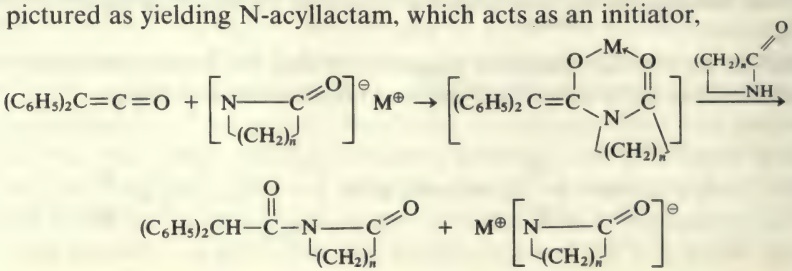
The work indicated that the metal aluminum alkyl reacts with the lactam to form a complex,



where M = Li; K; or Na, and X = C_2H_5 or a 2-oxoalkylene-imino group.

The complex is believed to increase catalyst solubility and also to protect polymer end groups from side reactions.

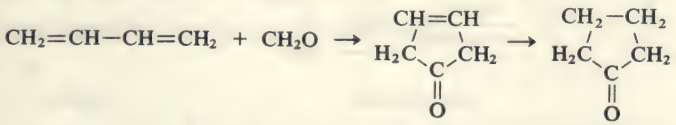
The reaction of diphenyl ketene with the alkali metal salt of the lactam was then pictured as yielding N-acyllactam, which acts as an initiator,



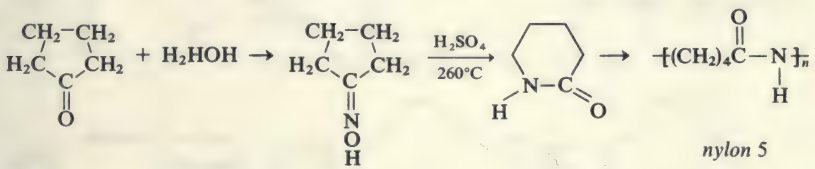
15-2. Common Nylons Formed by Lactam Polymerization

Synthesis of Nylon 5

Nylon 5 can be formed through the polymerization of valerolactam. This cyclic monomer can be synthesized from butadiene by reacting it with formaldehyde first to form cyclopentanone,



The cyclopentanone is then converted to the desired α-piperidine by the Beckman rearrangement of the corresponding oxime, and then polymerized to nylon 5.



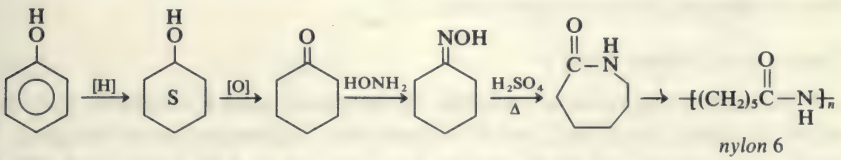
nylon 5

The polymerization of valerolactam requires the use of very pure monomer (*9*).

Synthesis of Nylon 6

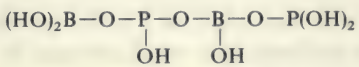
This polyamide is formed by the polymerization of ε-caprolactam. Owing to the considerable industrial importance of this polymer, a number of synthetic routes evolved for caprolactam preparation.

One such typical route starts with phenol,



nylon 6

Direct nitration of cyclohexanone appears to be another interesting route (*29*). This is done over a catalyst bed composed of

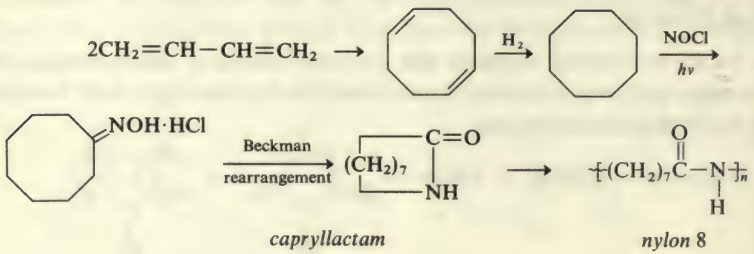


which is formed through the reaction of $2B(OH)_3 + 2P(OH)_3$.

Preparation of Nylons 8 and 12

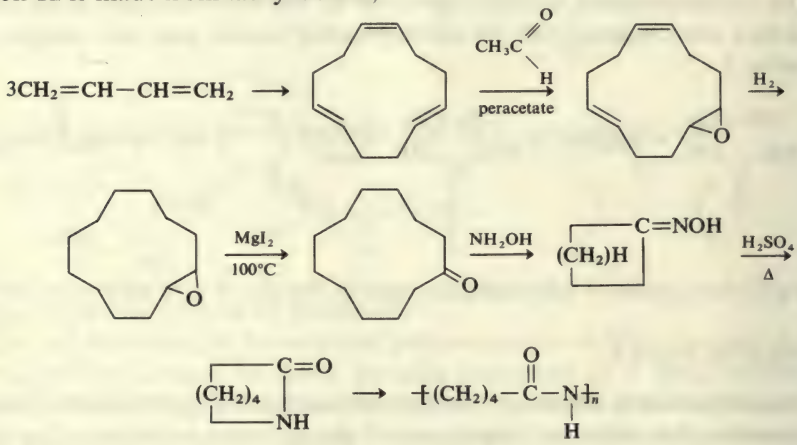
There is no economic commercial route to nylons 7, 9, and 10 by way of cyclic monomers. Nylons 8 and 12, however, are formed from the appropriate lactams. They are prepared from cyclic dimers and trimers of butadiene. Thus

caprylactam is formed as follows:



caprylactam *nylon* 8

Nylon 12 is made from lauryllactam,



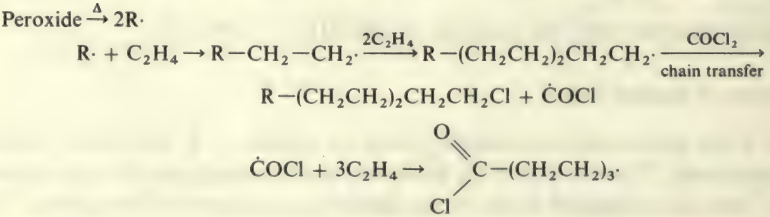
lauryllactam *nylon* 12

The polymerization of lauryllactam is carried out at very high temperatures. Almost theoretical conversions result.

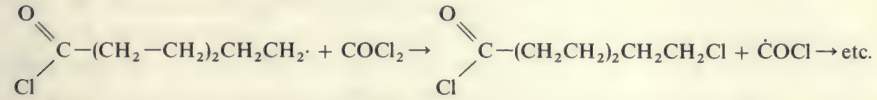
Syntheses of Nylons 7 and 9

A Russian process, developed by Nesmeyanov and Freundlina (*31*), is an industrial route to nylons 7 and 9. It starts with telomerization of ethylene. The reaction is carried out with oxygen or peroxides at 120–200°C and 400–600 atmospheres pressure. The preferred chain-transferring agents are CCl_4 or $COCl_2$.

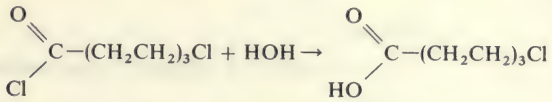
In the process, ethylene and CCl_4 or $COCl_2$ are introduced in the reactor in a ratio of 3:1 in the presence of a small amount (0.1–0.2%) of peroxide,



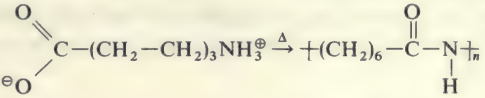
By the time a trimer is formed, the growing chain is expected to chain-transfer again,



The acid chloride trimer can be readily hydrolyzed,



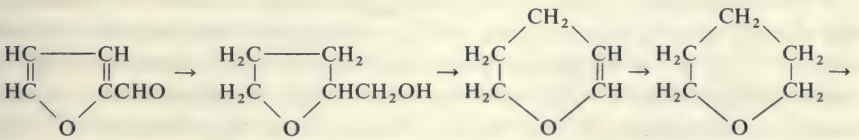
and then converted to the amino acid,



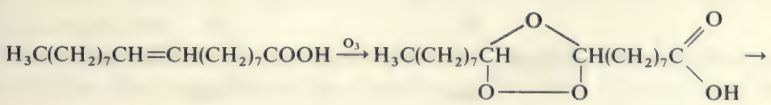
nylon 7

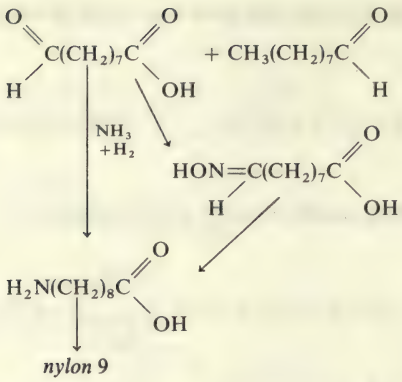
The telomerization process cannot be prevented from yielding tetramers, which are used to prepare nylon 9. Unfortunately, dimers and pentamers form as well, which detracts from manufacturing efficiency. The reaction is claimed to be controllable to yield 85% trimer.

This synthetic route can also be accomplished by carrying out the free-radical telomerization of ethylene in emulsion (*32*) using aliphatic amines in conjunction with copper salts as initiators. An alternative route to nylon 7 synthesis is via pyran,



Nylon 9 is also prepared through ozonolysis of oleic acid, a commercial process developed in Japan:



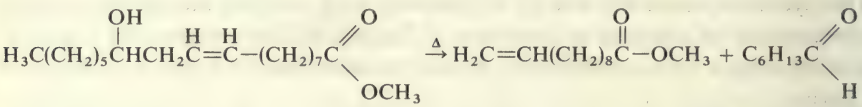


Nylon 10 is not presently prepared commercially in large quantities, as an economical route to nylon 10 does not appear to be fully developed as yet.

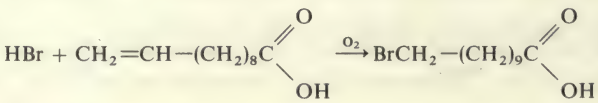
Synthesis of Nylon 11

Nylon 11 is synthesized on a large scale in France by Societe Organico. The polyamide is prepared from ricinoleic acid via 11-aminoundecanoic acid, which does not cycolyze into lactams because of its size.

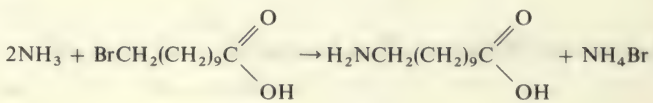
1. The methylester of ricinoleic acid is pyrolyzed to yield heptaldehyde and 11-undecylenic acid,



2. The undecylenic acid is then hydrobrominated counter-Markownikoff with the aid of nonpolar solvents, such as toluene-benzene mixtures and peroxides or oxygen. The Organico process makes use of packed columns, with the organic acid solution flowing downward and coming in contact with a counter-flowing-upward stream of HBr in air. This results in high yields (95–97%) of 11-bromoundecanoic acid,



3. The 11-bromoacid is then converted with ammonia to the corresponding amino acid,

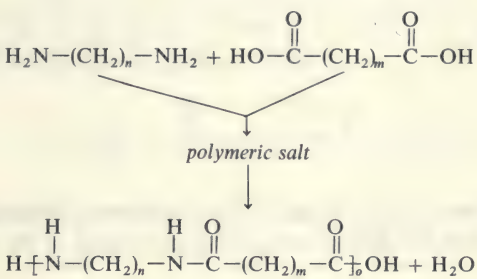


4. Polycondensation of 11-aminoundecanoic acid proceeds by simple heating of the molten monomer. Sometimes phosphorous acid or its derivative may be added to accelerate condensation.

The commercial preparation of nylon 13 from erucic acid found in Crambe seed appears a possibility for the near future. The erucic acid can be cleaved at its double bond by ozonolysis and then reductive amination used to yield the corresponding amino acid. This monomer can then be condensed to the polyamide.

15-3. Polyamides from Diamines and Diacids

This series of condensation polymers include every conceivable diacid and diamine. The reaction must be conducted in strict stochiometric quantities to achieve high molecular weights. Hot-melt conditions without the aid of any solvents are often used. First a salt is prepared, which is usually purified before further use.

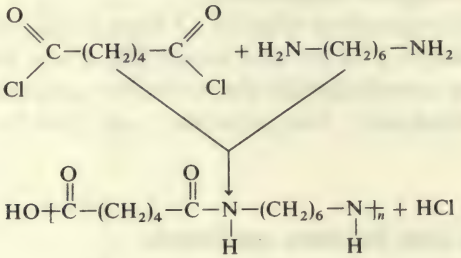


The condensation reaction can then be carried out without the aid of a catalyst. Usually the heating of the salt (*33*) is first carried out in a sealed vessel containing an inert atmosphere under pressure, to prevent loss of the usually volatile diamine and to attain formation of low-molecular-weight condensates. This can often be accomplished at about 215°C in $1\frac{1}{2}$–2 hours. Heating can then be continued under vacuum (0.2–1.5 mm Hg) at somewhat higher temperatures (about 270–280°C) for an additional hour to reach high molecular weights.

Obviously, variations of this technique are possible. Furthermore, various modifications of this high-temperature polycondensation are known. Thus (1) acid catalysts can be added to the melts of polymeric salt (*34*), (2) high-boiling solvents or plasticizers can be used to produce fluidity and permit condensation at lower temperatures (*35*), and (3) polymerization can be carried out in a finely divided solid state suspension (*36–41*) by dispersion of the salt in a nonsolvent (*42,43*).

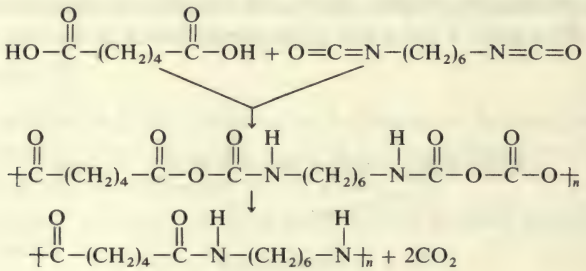
Furthermore, one can carry out the reaction by way of amonolysis of a diester by a diamine. The reaction can also be carried out at low temperatures by using

a diacid chloride in place of a diacid and a diamine by the technique of interfacial polycondensation (*43,44*),



nylon 6-6

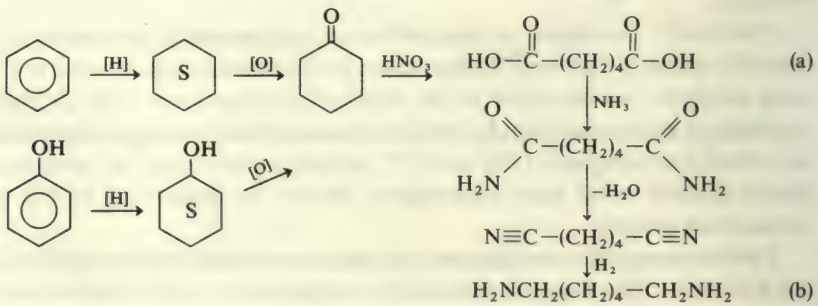
or between a diisocyanate and a diacid (*42*),



This last method has the advantage of the reaction proceeding at low temperatures and rapidly, but the disadvantage of higher costs of the starting materials.

Preparation of Nylon 6-6

Nylon 6-6 was first prepared by Carothers (*35*). Its synthesis was later described in detail by Coffman and co-workers (*45*). This polyamide has attained industrial importance. As a result, a number of synthetic routes exist today for the preparation of (a) adipic acid and (b) hexamethylene diamine. One can start, for instance, with benzene or phenol.



or one can start with butadiene,

$$H_2C{=}CH{-}CH{=}CH_2 \xrightarrow[\text{counter-Markownikoff}]{2HCl} ClCH_2{-}CH_2{-}CH_2CH_2Cl \xrightarrow{2KcN}$$

$$N{\equiv}C{-}(CH_2)_4{-}C{\equiv}N \xrightarrow{HOH} HO{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_4{-}\overset{O}{\overset{\|}{C}}{-}OH \qquad \text{(a)}$$

$$\xrightarrow{H_2} H_2N{-}CH_2{-}(CH_2)_4{-}CH_2NH_2 \qquad \text{(b)}$$

One can also start with tetrahydrofurane,

$$\begin{array}{l} H_2C\text{——}CH_2 \\ \quad|\qquad\quad| \\ H_2C\quad\ CH_2 \\ \quad\diagdown\ \ /\ \ \xrightarrow{2HCl} Cl(CH_2)_4Cl \xrightarrow{KCN} N{\equiv}C{-}(CH_2)_4{-}C{\equiv}N \rightarrow \text{etc.} \\ \quad\ O \end{array}$$

The synthetic process, as mentioned earlier, starts with the initial preparation of a 1:1 salt from the diacid and the diamine, which are combined in stochiometric amounts (*45*). This can be done by dissolving each separately in ethyl alcohol and then combining the two solutions. The salt will then crystallize out overnight. If needed, it can be isolated and further purified. Polymerization can then be conducted in two stages, as stated:

$$[\overset{\oplus}{H_3}N{-}(CH_2)_6{-}\overset{\oplus}{N}H_3][\overset{\ominus}{O}{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_4{-}\overset{O}{\overset{\|}{C}}{-}\overset{\ominus}{O}] \rightarrow$$

$$+N{-}(CH_2)_6{-}N{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_4{-}\overset{O}{\overset{\|}{C}}{+}_n + H_2O$$

$$\quad H \qquad\quad H$$

Nylon 6-10

Another industrially important polyamide is nylon 6-10. Here sebacic acid is used in place of adipic, otherwise using the same reaction conditions and molar quantities of the reactants,

$$[\overset{\oplus}{H_3}N{-}(CH_2)_6{-}\overset{+}{N}H_3][\overset{\ominus}{O}{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_8{-}\overset{O}{\overset{\|}{C}}{-}\overset{\ominus}{O}) \rightarrow$$

$$+N{-}(CH_2)_6{-}N{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_8{-}\overset{O}{\overset{\|}{C}}{+}_n$$

$$\quad H \qquad\quad H$$

nylon 6-10

Obviously, many diamines and diacids can be used for such polyamide formations, and actually to date an impressive number have been synthesized. However, most of them have not attained great industrial significance, perhaps because of unavailability of cheap starting materials or due to lack of desired physical properties.

Low-temperature or interfacial polycondensation of a diacid chloride and a diamine lends itself particularly well to preparation of polyamides. As a result this approach has been used in various laboratories to prepare a very vast number of such products. Morgan (*44*) lists nearly 300 polyamides prepared in this manner.

15-4. Physical Properties of Polyamides

Over the past 20 years many studies have been carried out on correlations of physical properties of polyamides with their microstructure. Coffman and coworkers (*45*) listed the variations of melting points of polyamides as influenced by the carbon chain length of the diamine used. Table 15-1 gives the melting points of a number of such polyamides. The melting points of polyamides derived from lactams or amino acids are listed in Table 15-2.

Hill and Walker (*46*) observed that in any one series the melting points of polymers containing only even numbers of $-CH_2-$ groups between polar links will lie on a different curve than do those of polymers that contain an odd number of $-CH_2-$ groups. The result is that the melting-point curves of homologous series (as we can see from Tables 15-1 and 15-2) of polymers have a zigzag form. This they explained (*46*) on the basis of the crystalline arrangement of polymer chains. A similar explanation was offered by others (*47*). The molecules of poly(hexamethylene adipamide) and poly(hexamethylene sebacamide) are arranged in sheets in such a way that —NH— of one molecule will be hydrogen-bonded to the —CO— of the neighboring molecule. By assuming this planar zigzag structure for all polyamides, Hill and Walker (*46*) draw a general picture. They assumed that in macromolecules with odd numbers of $-CH_2-$ groups, the amide linkages are so arranged that every —CO— group faces an —NH— group, allowing 100% hydrogen bonding and resultant high melting points. On the other hand, the even-numbered $-CH_2-$ groups

TABLE 15-1
Approximate Melting Points of Nylons
(In degrees centigrade)[a]

	No. carbon atoms, Diamine								
Diacid	2	4	5	6	7	8	9	10	11	12
Succinic		—	—	—	—	—	—	239	—	—
Adipic		278	223	250	236	235	205 (212)	230	—	209–210
Pimelic		233	183	202	196	—	—	—	—	—
Suberic		250	202	215 (220)	200	205	—	—	—	—
Azelaic		223	178	185	169	—	—	—	—	—
Sebacic		239	195	209–210	187	197	174	194	168	172

[a] From References *45* and *60*.

TABLE 15-2
Properties of Polyamides[a]

Monomer	Formula	Nylon types	Approx. m.p., °C
Acrylamide	$H_2C{=}CHC(=O)NH_2$	Nylon 3	320–330
Pyrrolidine	$H{-}N{-}(CH_2)_3C{=}O$	Nylon 4	
Valerolactam	$H{-}N{-}(CH_2)_4C{=}O$	Nylon 5	260
Caprolactam	$H{-}N{-}(CH_2)_5C{=}O$	Nylon 6	215–220
7-Aminoheptanoic acid	$H_2N{-}(CH_2)_6C(=O)OH$	Nylon 7	225–230
Capryllactam	$HN{-}(CH_2)_7C{=}O$	Nylon 8	195
9-Aminopelargonic acid	$H_2N{-}(CH_2)_8C(=O)OH$	Nylon 9	197–200
10-Aminodecanoic acid	$H_2N{-}(CH_2)_9C(=O)OH$	Nylon 10	173
11-Aminoundecanoic acid	$H_2N{-}(CH_2)_{10}C(=O)OH$	Nylon 11	185–187
Lauryllactam	$HN{-}(CH_2)_{11}C{=}O$	Nylon 12	180
13-Aminotridecanoic acid	$H_2N{-}(CH_2)_{12}C(=O){-}OH$	Nylon 13	173

[a] From various sources in the literature.

will allow for only 50% meeting of —NH— groups with —CO— groups and so only 50% of hydrogen bonding, with resultant low melting points. They draw an illustration of condensation products of diacids with diamines. This is shown in Figure 15-1.

A picture of nylons 6 and 7 is also shown by Ruland (*48*). In the crystalline forms of nylons 6 and 7 the chains are linked together by a regular array of hydrogen bonds that build up a two-dimensional network. These planes are stacked parallel to each other in such a way as to cause the assembly of hydrogen bonds to lie in planes perpendicular to the chain axis, in the case of nylon 6,

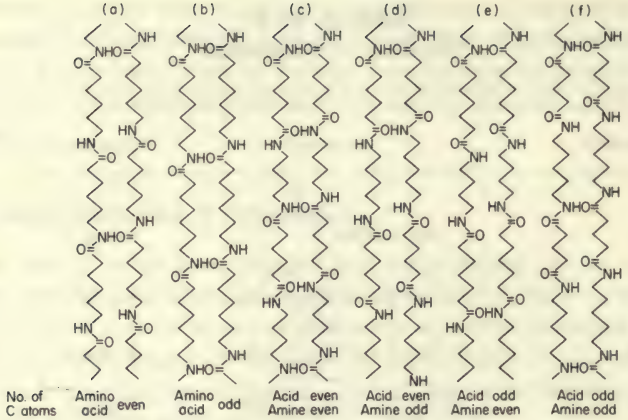
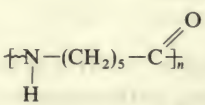


Figure 15-1. Effects of zigzag planar configuration on hydrogen bonding. (From Reference *46*.)

tilted in nylon 7. This difference is due to the fact that adjacent chains in polycaprolactam have opposite directions of amide linkages whereas in nylon 7 these sequences are in the same direction.

So in nylons 6 or 8 complete hydrogen bonding without chain distortion is possible only when adjacent chains have —CO—NH— sequences in opposite directions, whereas for nylon 7 these sequences can also be in the same direction. A complete hydrogen bonding in a noncrystalline state such as a quenched melt, for example, is thus possible without much strain in the case of nylon 7, whereas in the case of nylon 6 considerable twisting of chains is involved. This is illustrated in Figure 15-2. In the case of nylons 6 and 8, only 50% of the H bonds would form when chains are fully extended.

Actually there are at least two well-marked crystalline forms of polycaproamide,



One form, α, was investigated by Holmes and co-workers (*49*). They found that the polymer has a sheet structure of alternately directed fully extended chains connected by hydrogen bonds. These alternate sheets (or antiparallel sheets) are displaced along the chain axis, an arrangement that gives four chains in a monoclinic unit cell. A second form observed by Holmes et al. (*49*) was suggested to differ in the packing arrangement of the chains. He called this form the β form.

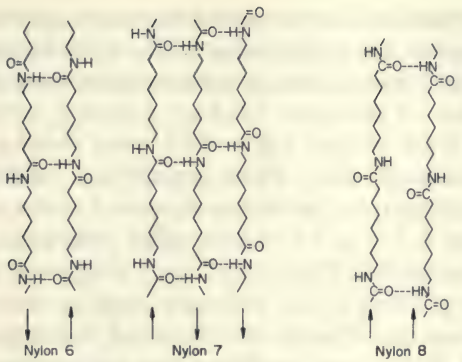


Figure 15-2. H bonding in nylons 6, 7, and 8.

Still another form, a γ form, was reported by Ueda and Kimura (*50*) and by Tsuruda et al. (*51*). This γ form was shown by Kinoshita (*52*) to be characterized by a somewhat controlled chain repeat length, compared with the fully extended form. He suggested that the hydrogen bonds in the γ form were formed between *parallel* chains and that a tilting of the amide groups occurred to form a linear hydrogen bond. As a result, the chains were somewhat contracted. This type of situation was actually well established by Kinoshita (*53*) in nylon 7, with X-ray crystallography.

The structure of the γ form of nylon 6 was later examined with X-ray diffraction by Vogelsong (*54*). He concluded that the γ form is identical with the β form of Holmes et al. (*49*). This was confirmed by Bradbury and co-workers (*55*).

Vogelsong points out, however, that generally antiparallel chain packing appears to be the common form of nylons 4 and 6. Parallel packing, on the other hand, appears to be the common form of nylons 8 and 10. Apparently, when sufficient flexibility is given to the even nylon chains by the addition of methylene groups, the twisted chain structure is favored.

15-5. Copolyamides

Copolymerization of polyamides can be achieved by combining salts of various monomeric species in the melt. This process alone opens the route to a very large potential number of materials. Furthermore, random copolymers are a type formed quite readily, because at the high temperature of the polymerization there is continuous interchange of reactive chain links.

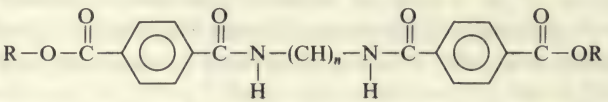
Low-temperature or interfacial polycondensations are also suited for copolymer preparation. Here, however, alternating and block copolymers form preferentially. Random copolymers, however, form with difficulty because of the inherent differences in reaction rates, diffusion rates, and solubilities. As a

result, although interfacial polycondensation was used to prepare a considerable number of copolyamides, few appear to be random copolymers (*44*).

Baker and Fuller (*56*) investigated systems prepared from aliphatic diamines and diacids. This class of materials was later extended further (*57*). Thus copolymers of nylon 6-6/6-10 and nylon 6-6/6 were developed, as well as a terpolymer of nylon 6-6/6–10/6. These copolymers exhibited considerable improvement in flexibility over the homopolymers. A series of copolymers and terpolymers of nylons 6, 6-6, and 6-10 with nylon piperazine-10 were reported by Hamilton and Epstein (*58*). These copolymers were found to possess a lower degree of crystallinity, owing to less hydrogen bonding because of piperazine. In addition, Hamilton and Questel (*59*) observed that terpolymers of nylon 6-6/6-10/pip-10 had the greatest stability when components were present in nearly equal proportions.

Besides carrying out copolymerizations of amides, one can also form polyester amides. Two types of such copolymers were described by Izard (*60*), the copolymers of hexamethylene sebacamide with hexamethylene sebacate, and the copolymer of *p*-xylylene sebacamide with hexamethylene sebacate.

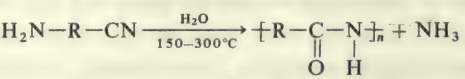
Polyester amides were also investigated by Williams and co-workers (*61*). They formed regularly alternating copolymers with glycol components ranging from C_2 to C_{14} and interamide linkages ranging from 2 to 6 by high-temperature polycondensation of preformed bisesteramides with sodium hydrogen tetrabutyltitanate as catalyst. The general structure of the bisesteramides was



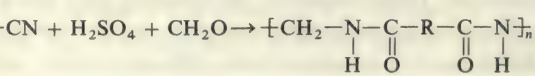
The bisesteramide was then condensed with a glycol via an ester interchange reaction.

15-6. Special Syntheses of Polyamides

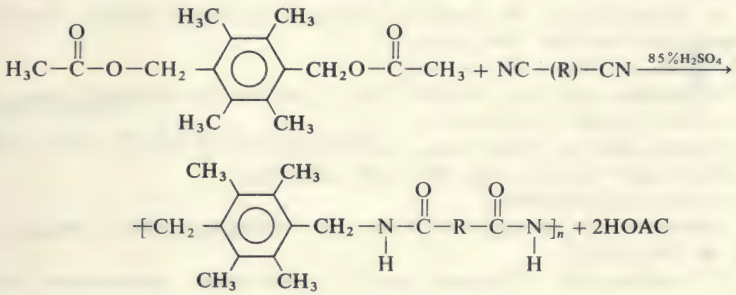
Greenewalt demonstrated (*62*) that one may form polyamides from aminonitriles when the reaction is carried out in the presence of water,



Magat demonstrated (*63–68*) that dinitriles can be condensed in the presence of sulfuric acid in the cold when a tertiary alcohol or formaldehyde is present which probably serves as a source of carbonium ions (Ritter reaction).



This use of the Ritter reaction to form polyamides was explored further by Ramp (*69*). He found that bis(acetoxymethyl) durene reacted readily with nitriles in strong sulfuric acid, yielding a series of interesting polyamides,



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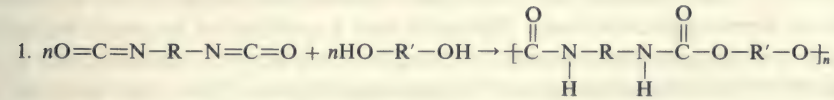
16

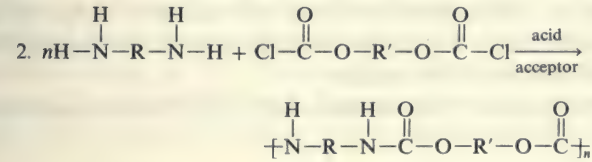
Polycarbamates, Polyureas, and Polycarbodiimides

16-1. Chemistry of Isocyanates

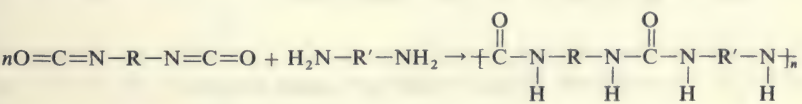
The polycarbamates, or as they are commonly referred to, polyurethanes, have come into much greater industrial use than the polyureas. They can be found in commercial fibers and plastics. By far the largest use of these polymeric materials, however, is in the form of block copolymers for coatings, adhesives, elastomers, and foams. In these applications the carbamate links are actually only a small part of the overall space-network structure of these materials, often acting as the final closing link for various prepolymers. This was the subject of several review articles (*1–5*) and two books (*6,7*).

The polycarbamate can be formed by two methods: (1) by a low-temperature solution polycondensation, and (2) by interfacial polycondensation. The first method requires a reaction of a diisocyanate with a diol and the second a bischloroformate with a diamine,





When the glycol, case (1), is replaced by a diamine, a polyurea results,



Reactions described in case (1) have by far the greatest industrial application in the formation of polyurethanes. As a result, the chemistry of isocyanates is quite important to the subject of urethanes.

The isocyanates can be synthesized by a variety of methods. One can, for instance, synthesize isocyanates from alkyl sulfates and potassium isocyanate, when R is a methyl or ethyl group (*8*),

$$R_2SO_4 + 2KNCO \rightarrow 2RNCO + K_2SO_4$$

Gautier (*9*) demonstrated that one can also oxidize isocyanides to the isocyanates with mercuric oxide,

$$RNC + HgO \rightarrow R{-}N{=}C{=}O + Hg$$

Slocombe and co-workers (*10a*) reported the use of phosgene as a convenient means for converting amines to the isocyanates. The reaction is conducted without the aid of a catalyst. This is based on work by Herman and Schmidt (*10b*):

$$CH_2NH_2 \cdot HCl + COCl_2 \xrightarrow{250°C} CH_3NHCOCl + 2HCl$$

$$2CH_3NHCOCl + 2CaO \longrightarrow 2CH_3NCO + CaCl_2 + Ca(OH)_2$$

Many modifications of this procedure have been devised since its original inception. Commercially, the isocyanates are usually prepared by reacting a solvent slurry of an appropriate amine hydrochloride with phosgene. Solvents most commonly used are ethyl acetate, toluene, *o*-dichlorobenzene, and nitrobenzene. The main drawback of this process is the low concentration of the amine salt which can be handled by such procedure.

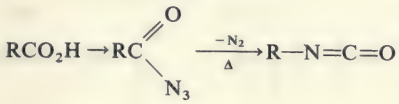
Irwin (*11*) developed a liquid-transport process which operates on a continuous or semicontinuous basis. Phosgene and a solution of aromatic primary amine in a halogenated aromatic hydrocarbon are added simultaneously to a solution of the desired isocyanate in the same solvent. The latter solution is maintained at solvent reflux temperature between 130 and 300°C. HCl and unreacted phosgene are constantly withdrawn through a reflux column while product is taken off at the bottom of the reactor.

A German process (*12*) is based on the carbonate salt route, which is superior to the HCl route:

$$H_2N(CH_2)_6NH_2 + CO_2 \rightarrow H_3\overset{\oplus}{N}(CH_2)_6NC\begin{matrix} H \\ \diagup\!\!\!= O \\ \diagdown \\ O^{\ominus} \end{matrix} \xrightarrow{2COCl_2}$$

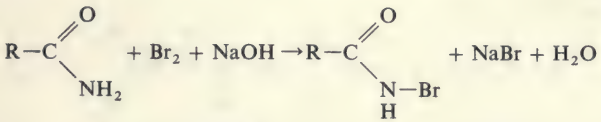
$$O{=}C{=}N{-}(CH_2)_6{-}N{=}C{=}O + 4HCl + 2CO_2$$

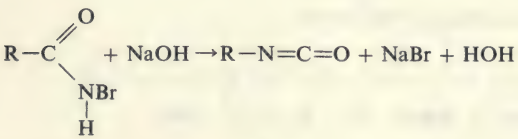
The well-known Curtius reaction is also a good means to isocyanate synthesis (*13*),



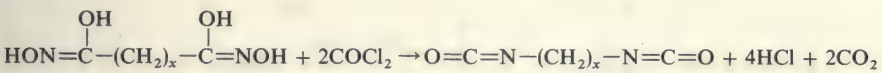
The rearrangement in benzene or chloroform is a very general method affording good yields.

The Hoffman rearrangement (*14*) is another method,

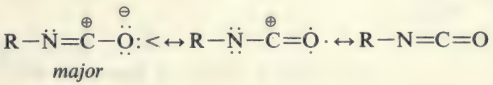




The Losson rearrangement (*15*) is still another,

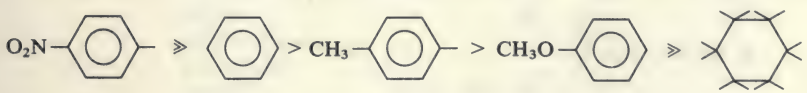


Reactionwise, the isocyanate molecule itself can be considered a resonance hybrid of three electronic arrangements (*16*) with the highest charge density on the oxygen and the least on the carbon,



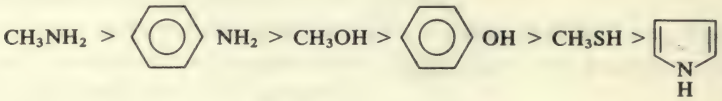
major

The reaction of an alcohol and an isocyanate involves an attack by a nucleophilic center upon the electrophilic carbon of the isocyanate. Any group that is attached to the isocyanate group and is electron-withdrawing will increase the positive charge on the carbon atom, thereby increasing the —NCO reactivity toward a nucleophilic attack. Conversely, electron-donating groups will reduce the —NCO reactivity toward a nucleophilic attack. We can write a comparison:



The reactivity of the nucleophilic agent attacking the electrophilic carbon of the —NCO group will increase as its nucleophilicity increases. Here, too,

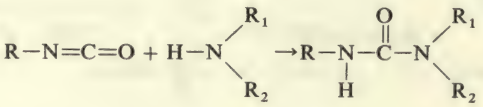
we can line up compounds according to their relative degrees of reactivity with isocyanates,



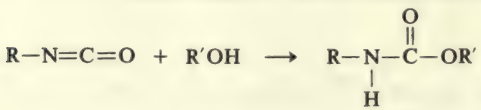
Steric factors must not, of course, be overlooked in any such consideration.

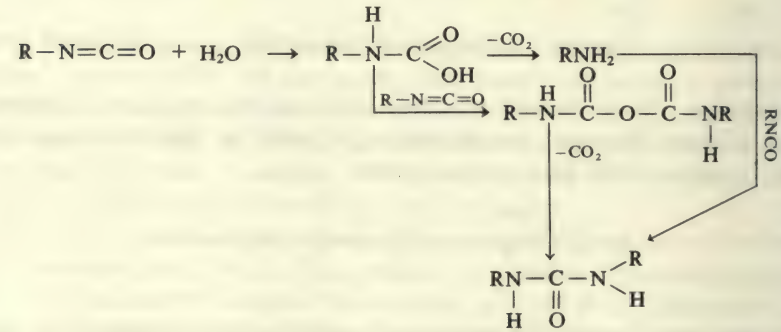
Typical reactions of isocyanates are as follows:

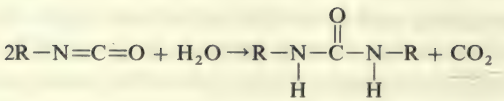
With amines:

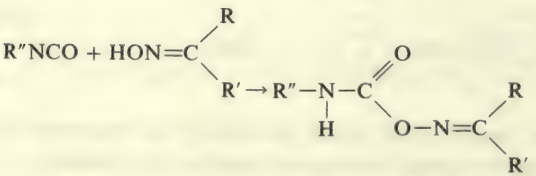


With oxygen-bearing compounds:

1. 

2. 

3. 

4. 

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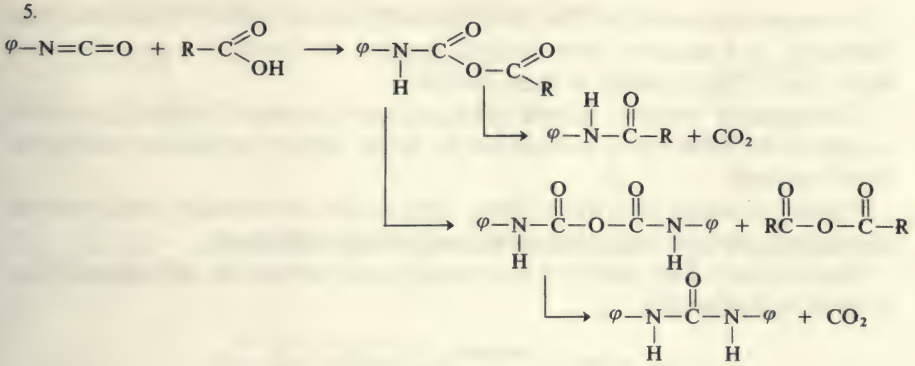

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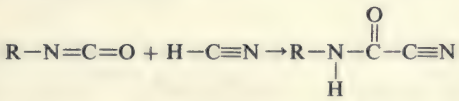

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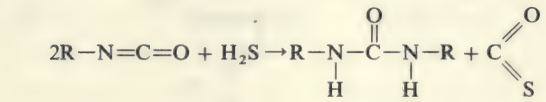

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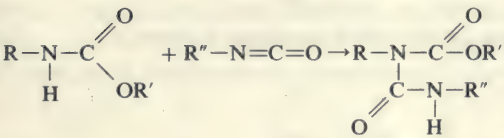
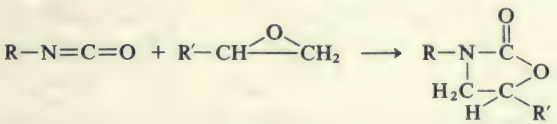


allophanate

9.



The relative reaction rates are given in Table 16-1.

TABLE 16-1

Relative Rates of Reaction with φ—N=C=O[a]

Reactant	Rate
N-Butylphenyl Carbamate	1
Amide	16
Carboxylic acid	26
Carbamide	80
Water	98–100
Alcohol	460–480

[a]From References *16* and *17*.

It is important to observe that reactivity with water is useful in polycarbamate chemistry, as a means to cross-linking, because the ureido nitrogen can react with other —NCO groups to form biurets.

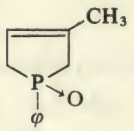
The urethane reaction is base-catalyzed, and in case of aliphatic alcohols appears to be inhibited to some extent by acids. Tertiary amines are among the better catalysts.

Primary alcohols react about three times as fast as secondary ones, whereas the tertiary alcohols react very slowly and tend to dehydrate.

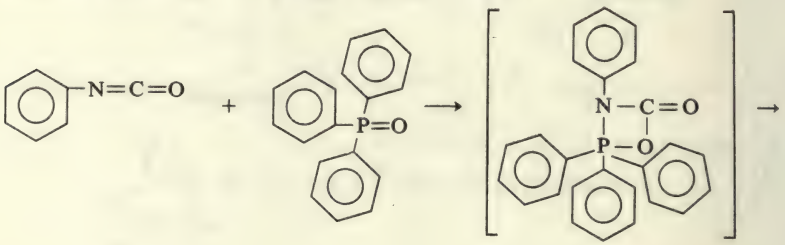
Dimerization: Two moles of isocyanates can combine by splitting off CO_2 to form carbodiimides:

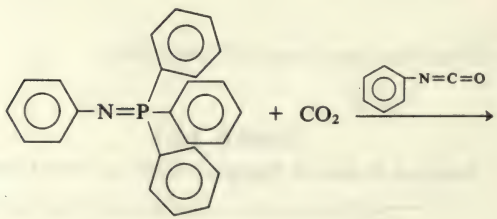
$$2\varphi\text{—N=C=O} \xrightarrow{\text{above } 40^\circ\text{C}} \varphi\text{—N=C=N—}\varphi + CO_2$$

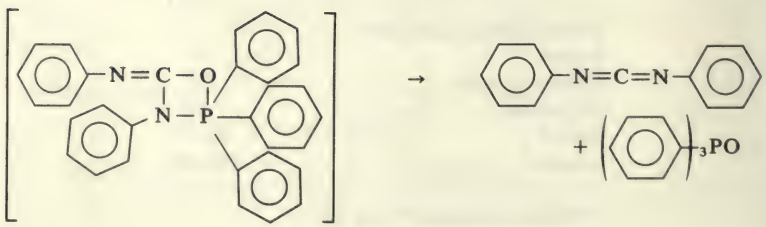
A typical catalyst for such a reaction can be 3-methyl-1-phenyl-3-phospholine oxide,



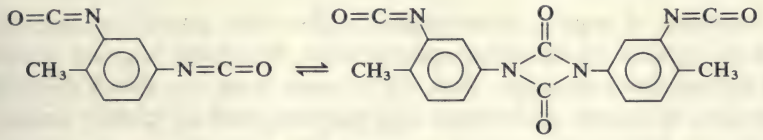
or triphenyl phospine oxide, which reacts as follows:



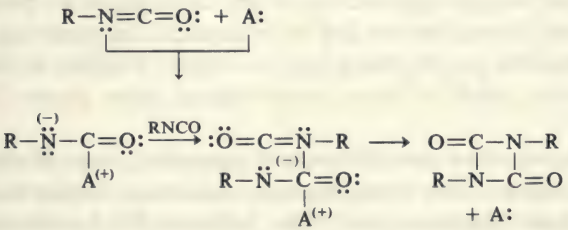




A typical dimerization is also an equilibrium reaction,

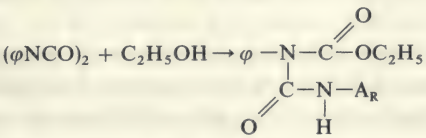


Various other nucleophilic agents are also catalysts for such a reaction. The probable mechanism can be shown as



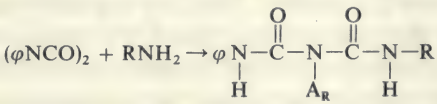
The availability of a pair of unshared electrons on the catalyst is in itself not sufficient, however, and here, too, structural or other factors must be involved.

Alcohols will react with the dimers to form allophanates,

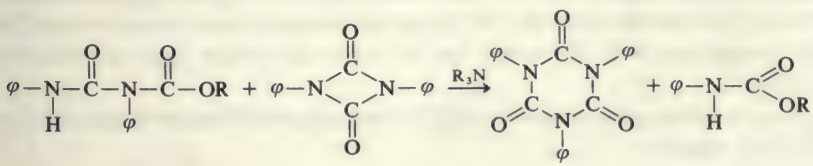


The reaction is slow, requiring prolonged heating of the dimer in alcohol.

Amines combine with dimers to form biurets,



Trimerization occurs only from reaction of an allophanate and a dimer and only occurs in the presence of a tertiary amine catalyst,



16-2. Polymer Preparation

The reactions of organic diisocyanates with either glycols or amines are sensitive to catalysis by the initial intermediates, by soluble reaction products, and by extraneous impurities. This can be seen from the above discussion. One can also, of course, deliberately add catalysts, such as tertiary amines or metal salts (*17–22*), to influence reaction rates. The secondary reactions between two or three isocyanate groups or between isocyanate groups with urethanes or with ureas will, of course, also be catalyzed by these materials. These secondary reactions are relatively slow. However, the best means for obtaining linear uniform polymers is to avoid use of any catalysts, when possible.

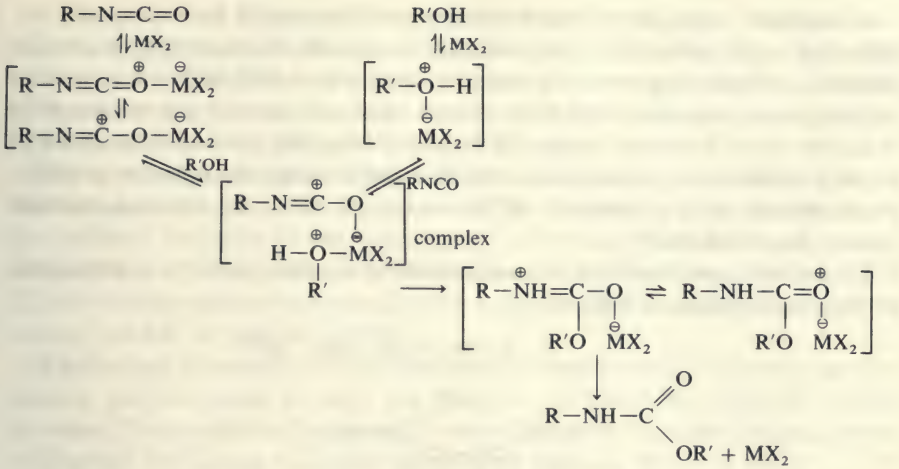
Dimer or trimer formation can also be responsible for upsetting the required stochiometric balance for obtaining high molecular weights. In the formation of polyureas, water tends to cause cross-linking when excess diisocyanates are present (*23*).

The synthetic procedure can often depend upon the proper choice of reaction conditions and solvent. Thus rapid mixing is recommended for those reactions which result in rapid precipitations of the polymer (*23*). For instance, to form a polycarbamate from ethylene glycol and diisocyanates, rapid mixing is necessary to attain high molecular weights (*24*). This may not be true for the formation of high-molecular-weight polyureas. Furthermore, to achieve high-molecular-weight polyurethanes it appears desirable to use inert true solvents for the polymer. This might also be the case for the preparation of polyureas (*23*).

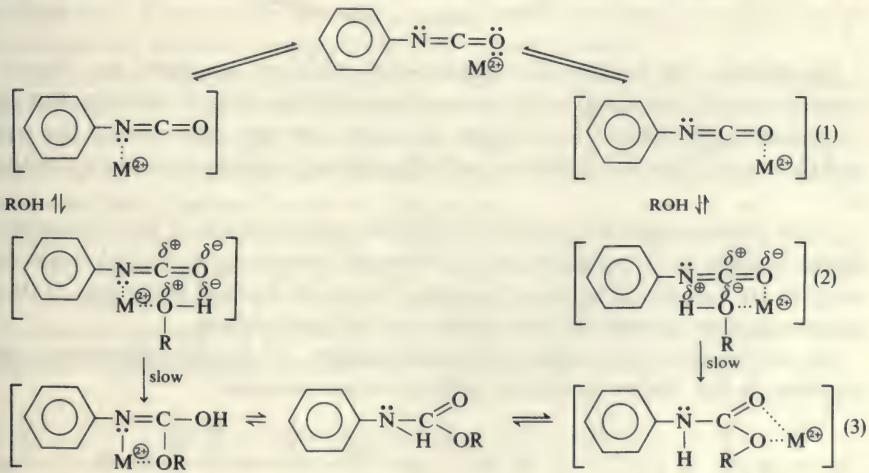
Britain and Gemeinhardt (*19*) observed that metal compounds, catalysts for formation of carbamates, fall into two major groups. Group 1 includes stannous, lead, bismouth, and organotin compounds, which appear capable of activating aliphatic isocyanates more than they do the aromatic ones, thereby making their reaction rates roughly equal. Group 2 includes zinc, cobalt, iron, tetravalent tin, antimony, and titanium compounds. These catalysts activate aliphatic isocyanates much more than the aromatic ones, thereby making them react faster than the aromatic isocyanates. This they explained on the basis of steric factors. In addition, they pointed out that if the metal compound lacks the ability to complex with incoming hydroxyl compounds and the isocyanate group in such a way that the hydroxyl group and the isocyanate nitrogen are brought closer together, then the catalytic activity will be due only to the acidity or basicity of the compound.

This suggestion was argued against by Smith (*25*), who pointed out that such a mechanism requires an attack of one electron-deficient center upon another, and would therefore be unlikely. He proposed instead a mechanism where the alcohol complexes with the metal ion at some site other than the reactive hydroxyl (*19,25*).

The two reaction schemes involving the formation of a ternary complex can be shown as follows:

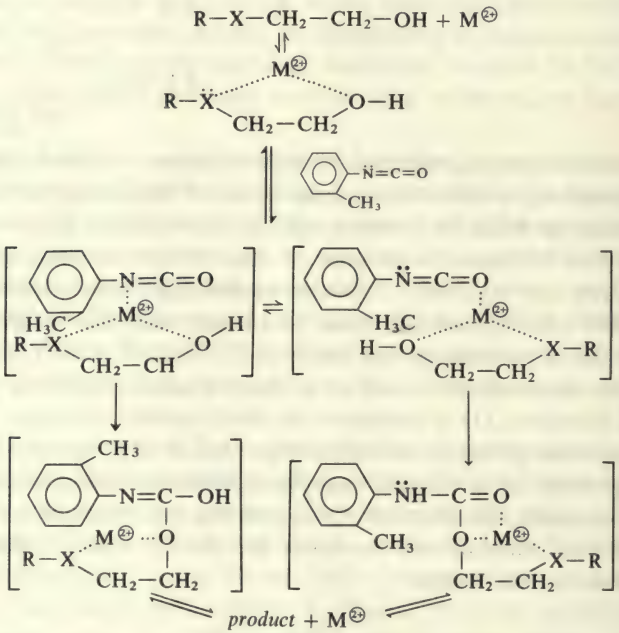


Robins (*26*) however, presented evidence in favor of a third scheme, a ternary complex involving a rather loose association of the isocyanate, metal ion, and the alcohol as the basis for catalytic activity of metal ions. He felt that the metal ions appear to fall into two groups: (1) those which maintain a fair portion of their catalytic activity even in systems containing hindered isocyanates (such as Pb^{2+}, Bi^{3+}, Sn^{2+}), and (2) those which are sensitive to changes in steric factors at the isocyanate group (such as Co^{2+}, Zn^{2+}, Cd^{2+}). This led him to suggest that the metal-ion catalysis of the isocyanate-hydroxyl reaction fulfills a twofold function: (1) it increases the electrophilic character of the carbon in the isocyanate group by coordinating either at the oxygen or nitrogen, and (2) it brings both the isocyanate and the alcohol in close proximity by forming a ternary complex. He therefore proposes two mechanisms, one for a simple monofunctional alcohol and the other for the "activated" alcohol. The first one he shows in this manner:



In the case shown above, the metal ion catalysts would have to satisfy the following requirements: (1) they should be capable of possessing a certain minimum complexing power in order to maintain a sufficient concentration of the ternary complex: (2) they should also not destroy the nucleophilic character of the hydroxyl oxygen to the extent that step (3) would be unlikely; (3) they should not, furthermore, complex tightly with the reaction product, which would cause a removal of the metal ion from the reaction mixture [render step (4) unlikely].

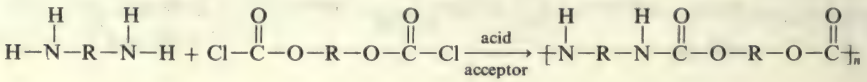
The second case, involving the mechanism of an active alcohol, is postulated by Robins (*26*) to be as follows:



In general, the fastest diisocyanate-diol addition reactions are those of aromatic isocyanates and aliphatic alcohols and the slowest between aliphatic isocyanates and phenol. In all these reactions, one can again expect the steric and electronic effects to influence both the primary and the secondary reactions (*27*).

Some observations were made (*24,28*) that a slight excess of the diisocyanate might actually be beneficial to polycarbamate formation, when high molecular weights are sought. This was explained (*28*) on the basis of some loss of diisocyanate groups by hydrolysis to amines or by dimerization.

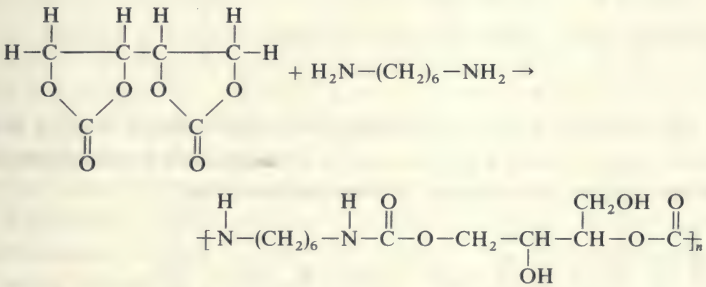
As mentioned, interfacial polycondensation of bischloroformates with diamines is the other convenient path to polycarbamates,



The reaction rate is reported to be slower than that of polyamide formation (*29,23*) although fast enough to reach completion in a few minutes when adequate stirring is used. The preferred solvents for such a condensation are benzene and dicholoromethane, with the presence of a detergent in the reaction mixture believed to be essential for good results (*30*).

Still another route to polycarbamates is via interfacial polycondensations of bis(carbamyl chlorides) with diphenolates. The drawback to this method is the low order of reactivity of the bis(carbamyl chlorides). Preparation of a polyurethane was reported, however, from piperazine-1,4-dicarbamyl chloride and 2,2-bis(4-hydroxyphenyl) propane, which melted at 230°C and had the inherent viscosity of 0.41 in *meta* cresol (*31*).

Whelan and co-workers (*32,33*) reported the preparation of hydroxyl-group-bearing polyurethanes through the reaction of bis(cyclic carbonates) with diamines. Thus erythritol dicarbonate was reacted with hexamethylene diamine in dimethyl formamide to form a low-melting polymer of $\eta_{red} = 0.4$.



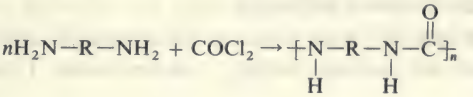
The same reaction was also applied to bis(2,3-carbonatoglycerol) and diamines with similar results.

When polyureas are formed by the reaction of a diisocyanate and a diamine, high temperatures are often employed throughout the condensation or as a finishing step. The reaction is usually carried out in solution. Interfacial polycondensations, however, appear to be quite useful as well.

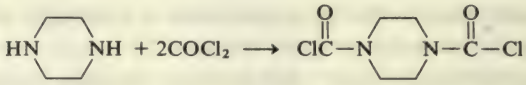
Here, too, the aliphatic diisocyanates are much less reactive than the aromatic ones (*17,18,34,35*). This shows up in the differences in the length of time required to carry out the reaction. The aliphatic diisocyanates are reactive enough, though, to form polyureas with primary diamines fairly rapidly. The reaction with secondary diamines, however, is quite slow.

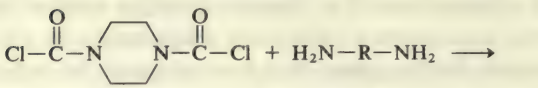
Because of the ability of residual isocyanates to react with ureas (see above), Katz (*36*) recommends washing freshly prepared products with boiling water for 5 minutes to destroy any reactive isocyanate groups left.

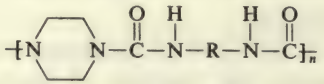
Polyureas can also be prepared quite readily by condensing diamines with phosgene. Interfacial polycondensation technique can be used here (*37,38*),



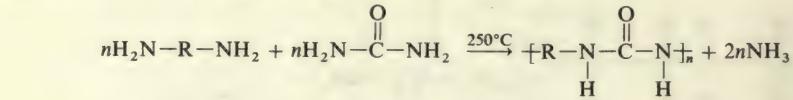
One can also pre-react a diamine with phosgene and then condense the formed carbamyl chloride with another diamine. By this method one forms alternating polyureas,



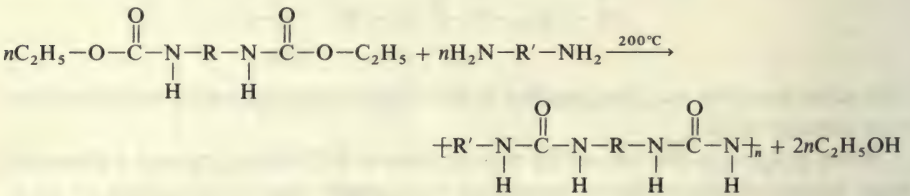




In addition, it was also demonstrated (*39*) that urea itself can be condensed with diamines to form a polymer by eliminating ammonia,



Finally, one can carry out aminolysis of a dicarbamate with a diamine as still another way to form a polyurea (*40*). This reaction is analogous to one that can be carried out on a diester to form polyamides.



16-3. Properties of Polycarbamates

Polyurethanes are not too stable thermally, at least not as stable as the polyamides (*41–44*). They will decompose above 200°C (particularly when metals are present). This puts a limitation on the processability of polyurethanes which have high T_m's.

In addition, polyurethanes prepared from ethylene glycols fail to yield satisfactory polymers, as they tend to decompose even upon melting. Those prepared from 1,3-propylene glycols and higher homologs, however, are more satisfactory. Glycols possessing secondary hydroxyl groups will usually yield low-melting, thermoplastic, and thermally unstable polymers, which are not suitable for use as films. Insertion of benzene rings in the chain results in more brittle and poorer-fiber-forming polymers.

Polycarbamates prepared from a given diisocyanate and a homologous series of glycols show alternating melting temperatures. Those formed from

glycols with an odd number of carbon atoms melt lower and are much clearer in films than those with an even number of carbon atoms.

Aliphatic polyurethanes melt generally lower than the corresponding members of other condensation polymers, with the exception of polyesters.

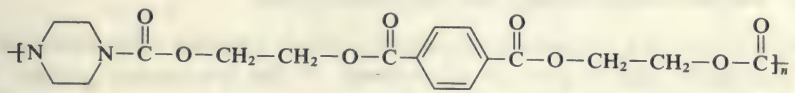
Lyman reported (*45*) that when a comparison was made of polycarbamates prepared from *cis* and *trans* glycols (such as *trans*-1,4-dihydroxy cyclohexane), the products from the *trans* isomers were higher melting, less soluble, and more dense. This is similar to Bunn's suggestion (*46*) for isoprenes— that geometrically enhanced flexibility due to inclined rotating bonds is the cause of the differences in melting points between *cis* and *trans* polyisoprenes.

In general, polyureas are higher melting than polyamides, but are quite susceptible to degradation, which limits their usefulness.

16-4. Copolymers of Urethanes

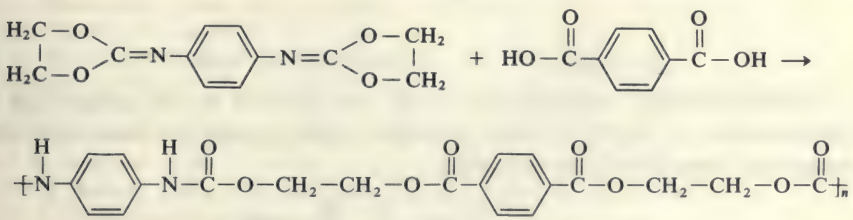
Copolymerization of urethane-forming intermediates is influenced by the relative reactivity of the coreactants, their availability at the reaction site, and the solubility of the polymeric products in the reaction medium. Not many random copolymers are reported in the literature. Those that are (*47*) were prepared by interfacial polycondensation, where the copolymer was a random polyamide-urethane copolymer.

There are several reports in the literature of alternating poly(ester urethanes). Thus Wittbecker (*48,49*) converted bis(hydroxyethyl) terephthalate to the bischloroformate with phosgene. The product was then reacted with piperazine, using interfacial polycondensation technique to form the copolymer.



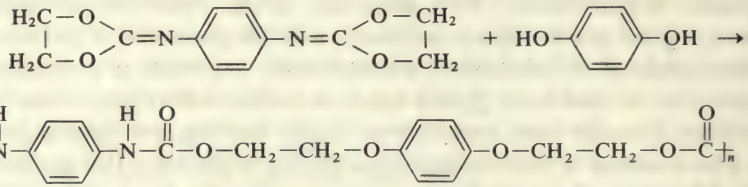
The copolymer melted at 215°C and had an inherent viscosity of 1.26 in *m*-cresol.

Mukaiyama and co-workers (*50*) formed alternating poly(ester urethanes) by reacting bis(imino cyclic carbonate) with adipic and terephthalic acids.



The reaction was achieved by heating intermediates in dimethyl formamide for 2 hours at 80°C. The adipate melted at 140°C, and the terephthalate at 236°C.

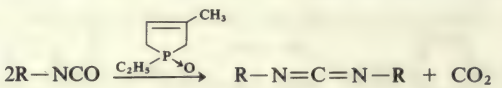
Hydroquinone was used (*51*) in a similar reaction to form a poly(ester urethane),



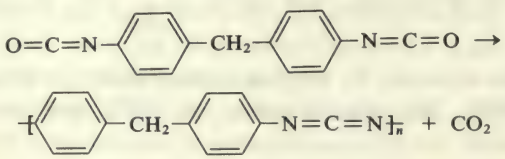
Block copolymers of polyurethanes on the other hand, have received extensive study, as many of these materials are commercially useful elastomers. Thus large-chain polyesters are chain-extended with diisocyanates to form many so-called *urethane rubbers.* Linear, aliphatic polyesters, such as, for example, condensation products of ethylene glycol and adipic acid, can be used. This low-melting, waxy solid will form an elastomer upon reaction with hexamethylene diisocyanate. "Vulcanization" or cross-linking to a cured rubber can then be attained by further addition of a diisocyanate or by reactions with formaldehyde-liberating agents in the presence of catalysts (*52*). In place of the polyesters one may use aliphatic polyethers (*53*). Similar block copolymers of poly(ester urethanes) and poly(ether urethanes) are used to form foams, which may be rigid as well as elastic. Here advantage can be taken of the CO_2 formation from the reactions between the isocyanate groups and water or carboxyl groups to form the foam. This is an expensive method for creating bubbles, however, and foaming is usually achieved by whipping in air, freon gas, or CO_2.

16-5. Polymerization through the Isocyanate Group

Polymerization reactions of isocyanates which received most attention are the hydrogen-transfer type condensations of the isocyanate groups with alcohols and amines. One can form polymeric systems, however, through the self-condensation of the isocyanate links (as in reactions of dimer formations). Thus Campbell and co-workers (*54–56*) utilized the catalyzed condensation reaction of isocyanates by converting them to carbodimides,

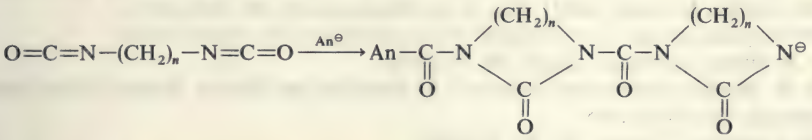


1-Ethyl-3-methyl-3-phospholine oxide was utilized as the catalyst in the condensation in inert solvents. High-molecular-weight polymers that were tough and crystalline formed readily,

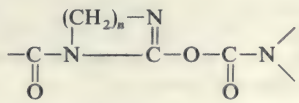


The polymers could be molded into clear films. Chemically these materials were quite inert when in the solid state. When swollen in solution, however, they tended to react with active hydrogen compounds to form different heteropolymers, such as, for example, high-molecular-weight polyguanidines.

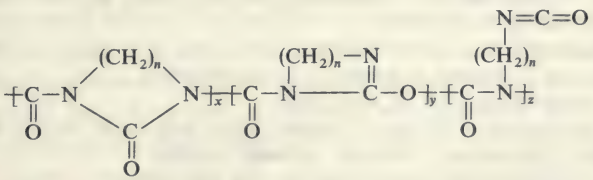
Iwakura and co-workers (*57*) carried out cyclopolymerizations of α–ω-polymethylene diisocyanates with basic catalysts in polar solvents, forming soluble products. These polymers were shown to contain heterocyclic recurring units (imidazolidone and imidazoline) in each chain. An intermolecular-intramolecular propagation mechanism was postulated which would lead to



Where $An^{\ominus}$ is the initiating anion. They found, however, that, in addition, another recurring unit,



was also present. So they concluded that the average structure of the products was



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Phenoplasts

17

Phenol and formaldehyde will condense readily to form polymers consisting of aromatic rings linked together by methylene or oxymethylene bridges which occur primarily in the *ortho* or *para* positions to the phenolic hydroxyls. These condensations are usually carried to the point of soluble metastable intermediates, which are later converted to infusible and insoluble three-dimensional structures by the addition of heat and in some cases also by the addition of more formaldehyde and catalyst.

Von Bayer was the first to observe this reaction of phenol and formaldehyde, in 1872. Much work was carried out on the condensation since then, especially after Baekeland discovered methods for utilizing the products as molding resins. Several books have been published on this subject (*1–4*).

In discussing the chemistry of phenol-formaldehyde polymers, Megson points out (*4*) one important difference between these condensation products and other typical macromolecules—that these materials are actually very complex mixtures of position isomers. Thus, for instance, even at low molecular weights, polymers composed of 10 phenolic units combined by methylene bridges through *ortho* or *para* positions are estimated to be capable of 13,203 linear isomeric structures alone (*5*).

In these condensations phenol is a trifunctional molecule and formaldehyde a difunctional one. The reactive positions of phenol are *ortho* and *para*, so substitution in the *meta* position by alkyl groups does alter the functionality of phenol. This will be an important point to remember in the consideration of reactions of substituted phenols with formaldehyde. *Ortho* or *para* substitution, on the other hand, changes the functionality of phenol, with the result that the condensation can only yield linear polymers.

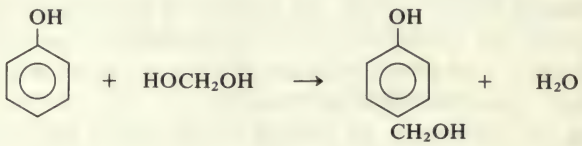
Condensation of phenol and formaldehyde is possible without the aid of catalysts, when carried out at higher temperatures, such as 140°C or even higher (*6*). Such reactions, however, are slow at lower temperatures and, as a result, catalysts are usually employed. These catalysts can be either bases or

acids. The products from the two will differ. The base-catalyzed condensations are thermosetting, so-called "one-stage" resins, and bear the name *resols*. The acid-catalyzed reaction products, on the other hand, are thermoplastic, "two-stage" resins, and are called *novolacs* (novolaks in England). To thermoset novolacs, an additional step is required, with more formaldehyde and catalyst added.

17-1. Resoles

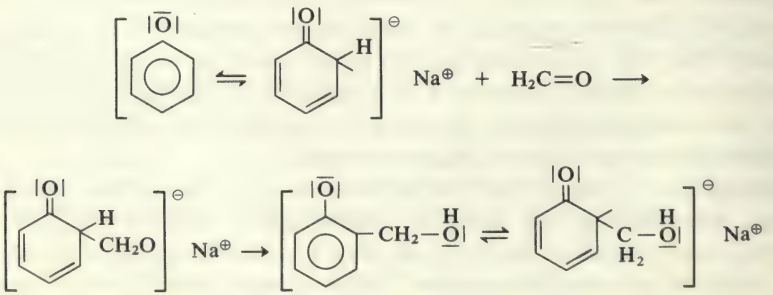
These resins are formed from reactions of formaldehyde and phenol, with the molar ratio exceeding 1:1, and often as high as 1.5:1. Almost any alkali can be used to achieve condensation. This is also true of alkaline-earth hydroxides, ammonium hydroxide, and amine bases. Ammonium hydroxide or amine catalyzed condensations differ, however, in the nature of the reaction products from the other resols and will have to be discussed separately.

When phenol and formaldehyde are combined in water under basic conditions and heat applied, *ortho* and *para* phenol alcohols form in the early stages of the reaction. Lederer and Manasse (*7*) were the first to observe this reaction. Manasse suggested that formaldehyde might be reacting in aqueous solution as methylene glycol,

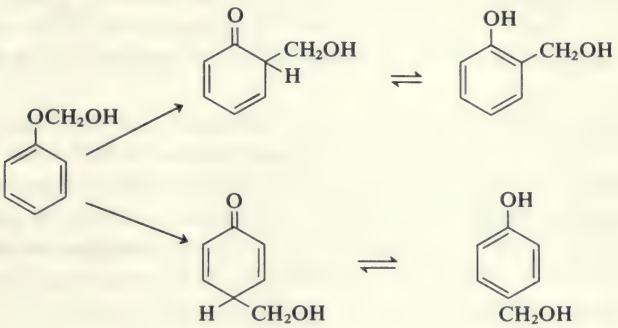


This idea was later modified by Manasse, and he preferred to think of the reaction as an aldol type condensation leading to alcohol groups.

Present-day thinking (*2*) is more toward the mechanism proposed by Hultzsch (*8,9*). The reaction is pictured as occurring because of the nucleophilic nature of the phenate ion and being dependent on hydroxyl ion concentration,



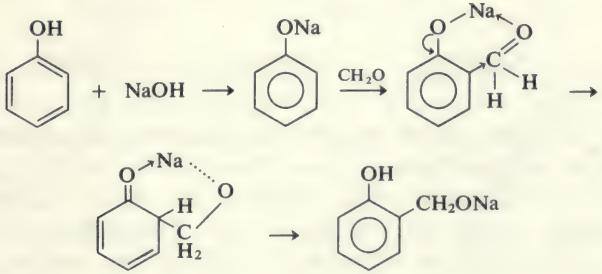
Walker prefers to think of the reaction intermediate as one involving a hemiacetal (*10*) which undergoes a tautomeric rearrangement,



Walker bases his thinking on the analogy between phenol alcohol formation and the formation of methylol products from reactions with aldehydes and ketones. Thus, for instance, it was shown that acid-catalyzed reactions of phenol and formaldehyde (in the form of formalin, with methanol present) can lead to the formation of methyl phenyl formal (*11,12*).

Also, phenol stabilizes formaldehyde against undergoing a Cannizzaro reaction under alkaline conditions used [unless half a mole of caustic is present per mole of phenol used (*2*)]. This would tend to support the idea of an initial acetal or hemiacetal formation, followed by a subsequent rearrangement to the phenol alcohol.

It appears quite certain that the presence of a phenolic hydroxyl group is necessary for the reaction. This is based on the fact that methylated or acetylated phenols react with great difficulty. Caesar and Sachauen (*13*) tried to explain the role of the phenolic hydroxyl group in alkali-catalyzed reactions by suggesting the formation of a chelate group with a subsequent intramolecular rearrangement which yields alcohols,



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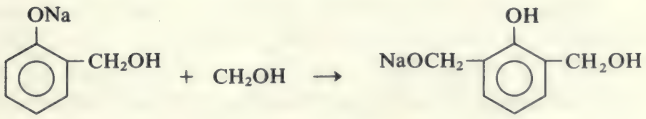
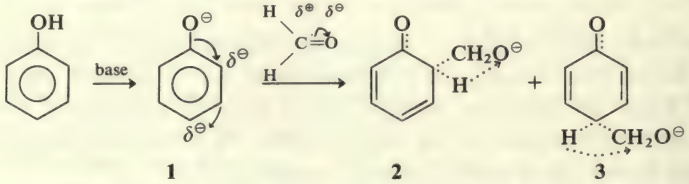


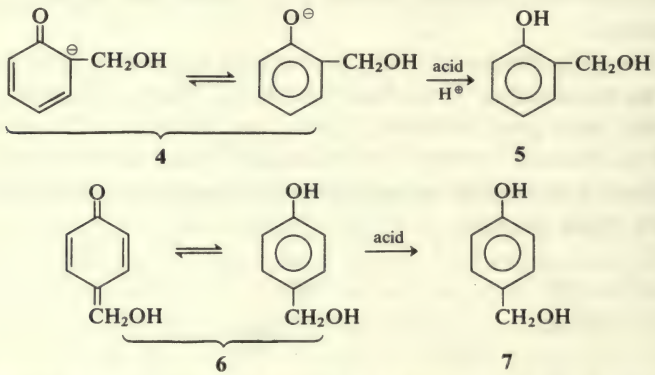
Megson (*4*) brings up three strong objections to this: (1) chelation cannot account for the well-established formation of the *para* methylol phenols, (2) there is very little concrete evidence that the phenolic hydroxyl group does indeed participate in the reaction, and (3) it has been demonstrated that in an alkaline medium some phenols will form dihydroxydiaryl methanes as well as alcohols of the latter.

Probably the most typical present-day explanation for the reaction of phenol with formaldehyde in the presence of a basic catalyst which leads to *ortho* and *para* derivatives of phenol is given by Royals (*14*), who refers to this as the Lederer–Manasse reaction. He pictures phenol as being converted to the phenoxide anion in the presence of a base similar to the explanation of Hultzsch (*8,9*). An electrophilic attack by formaldehyde on the phenoxide ion at the *ortho* and *para* positions leads to reaction intermediates (**2**) and (**3**):

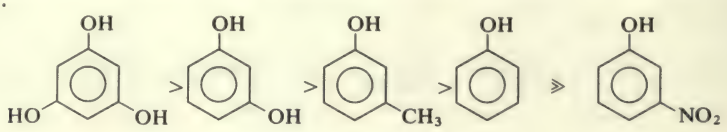


1 **2** **3**

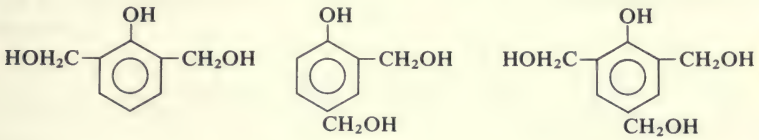
Structures (**2**) and (**3**) are transition states. Hydrogen transfer, inter-, or perhaps more probably, intramolecularly, leads to resonance structures (**4**) and (**6**):



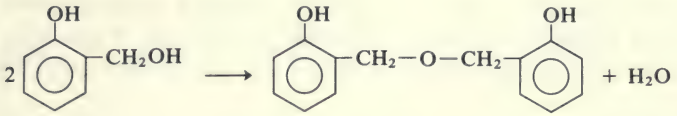
The influence of the substituent groups in the nucleus is quite strong, affecting the rate and the degree of condensation. Thus substitution in the meta position by an *ortho–para* directing group enhances the rate of the reaction. *Meta*-directing groups, on the other hand, will have a retarding effect on the rate. The substituted phenols can be shown in order of their relative reactivities as follows:



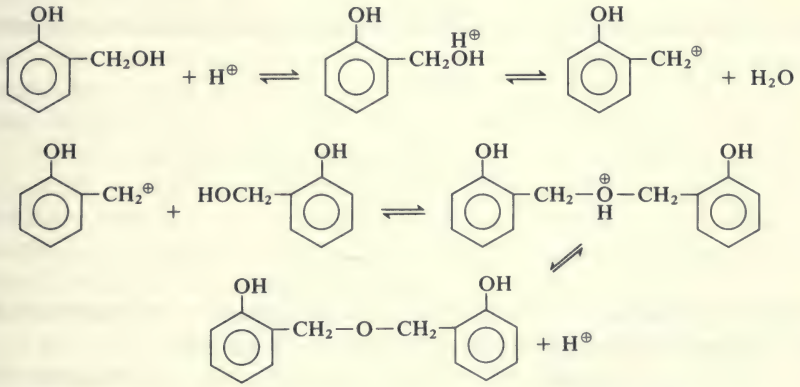
When the reaction of phenol and formaldehyde is not carried to a high degree of condensation, it is possible to isolate three di- and trisubstituted adducts:



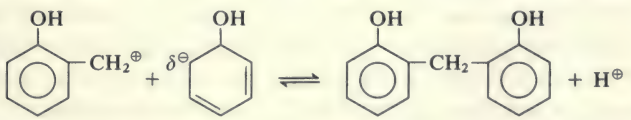
Meta substitution has never been observed (nor fully ruled out). As the condensation reaction progresses, the phenol alcohols can undergo self-condensation, some with the accompanying formation of dihydroxydibenzyl ethers,



The mechanism for ether formation was suggested by Lilley (*15*). He pictures the mechanism which occurs in the early stages, while water is still present and the resin has not separated out and is still in solution as being ionic,



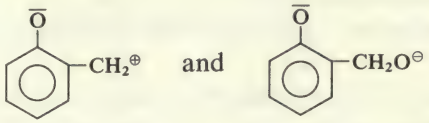
However, as the resin grows in molecular size and precipitates from the water at the later stages of the reaction, condensation occurs in a water-free medium (within the resin) and at a lower pH. A different route is then pictured:



with the resultant formation of methylene bridges rather than ethers.

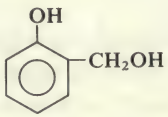
Megson feels (*4*) that by studying the concentration of carbonium ions (which controls the reaction) as the proton concentration is varied, one can demonstrate that under acidic conditions methylene bridges should be more

likely to form than ether linkages. In alkaline conditions, on the other hand, the concentration of carbonium ions will be low, but by considering the formation of these ions instead,

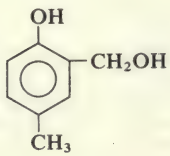


a similar conclusion can be reached. So he concludes (*4*) that the ethers should form only within a limited pH range and then only at slow rates, thereby precluding the likelihood of formation of large quantities of ethers.

Experimental evidence indicates that fully blocked monoalcohols lead to dibenzyl ethers in good yields, but this might not be true of partially or non-substituted phenols. Ziegler (*16*) was able to form ethers from saligenin,

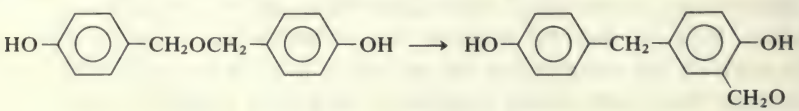


but only with difficulty. Von Euler *et al.* (*17*) had similar difficulty with homosaligenin,

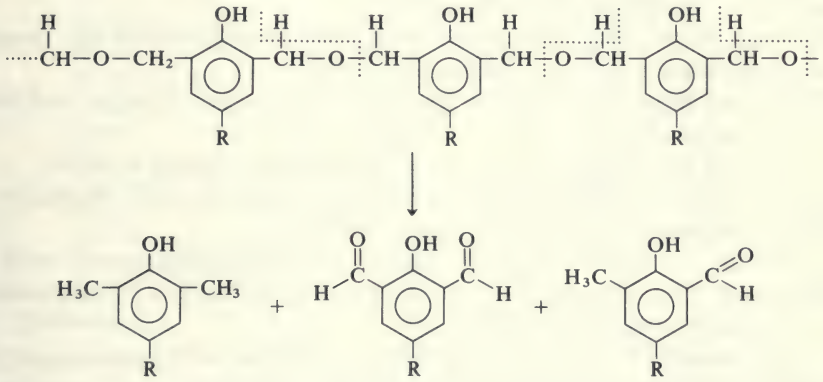


Nevertheless, Martin (*2*) feels that ether formation can play an important part in the cure or hardening of certain types of phenolic resins.

As we have seen, the dibenzyl ethers can be either the end products of the condensation of the phenol alcohols or the intermediate. The ease of formation as well as the tendency of the ethers to undergo further reaction will depend upon substitution on the benzene ring (*2*). The more active phenol alcohols are capable of being converted to dihydroxydibenzyl ethers at temperatures as low as 70–100°C in a resin melt (*18*), if the pH is not too high. Under special conditions, ether formation was even reported at room temperatures (*19,20*). Furthermore, Zinke (*21*) showed that heating of ethers results in splitting out of formaldehyde, which then tends to react with other positions,



Zinke (*21,22*) also isolated some methoxy materials from fully cured resins by pyrolysis, indicating that some attack occurs in the phenolic hydroxyl groups as well. He also obtained traces of dimethyl groups formed apparently by cracking,



Hanus and Fuchs (*1*) tabulated the temperatures at which *para*-substituted phenol alcohols lost water and formed ethers, and then lost formaldehyde from the ether group. This is shown in Table 17-1.

Martin concludes (*2*) that from all the available information it is possible to draw some generalizations about the formation of dibenzyl ethers and their importance in molecular growth during the condensation of phenol and formaldehyde.

1. When essentially neutral conditions exist, such as might be assumed to exist in the resin after a high-enough molecular weight is reached, and after separation from water, ether formation appears prominent with trifunctional phenols and of major importance during condensation of phenol alcohols formed from *ortho* and *para* alkyl phenols.

2. Acids as a rule depress the formation of dibenzyl ethers (as we shall see in the formation of novolacs). Small amounts of acids, however, may accelerate ether formation if an inactive phenol alcohol is involved.

3. Ether formation appears to be almost completely eliminated under alkaline conditions. This is true of phenol alcohols from phenol and from *ortho*- and *para*-substituted phenols.

And, as was shown by Zinke (*21*), dibenzyl ethers, in addition to being unstable in acidic and alkaline conditions, are also heat-labile. Temperatures above 160–170°C will cause decompositions and rearrangement to methylene bridges. Thus the chemical structure of the final product from condensation of phenol and formaldehyde will depend to a great extent upon the reaction conditions used.

The overall preparation of resoles can be described as occurring in three stages:

A stage. Phenol alcohol and some methylene ethers or methylene derivatives.

The reaction products might reach molecular sizes consisting of as many as six or even seven groups but are still soluble in aqueous alkali.

B stage. The reaction products now are so large that they no longer will dissolve in aqueous alkali but are still soluble in organic solvents. The polymeric material is a thermoplastic, brittle resin.

C stage. At this stage of reaction, large amounts of cross-linking occurred, and the polymer is no longer fusible or soluble.

Zinke and Ziegler (*23*) describe alkaline condensation of phenol and formaldehyde as follows:

1. Resoles are mixtures of mono- and polynuclear phenolic alcohols.
2. The primary reaction of hardening such alcohols is the formation of bridged compounds by the elimination of water.
3. During the further course of hardening, the ether bridges split with the evolution of formaldehyde to give, in part, methylene bridges. Their formation is encouraged by the presence of alkali.
4. The primary-formed ether partially decomposes under heating to yield phenolic aldehydes and methylated phenols.
5. It is believed that at higher temperatures particularly, quinone methides and their transformation products are formed.

From all this one can draw a structure of a resole in the C stage in this manner:

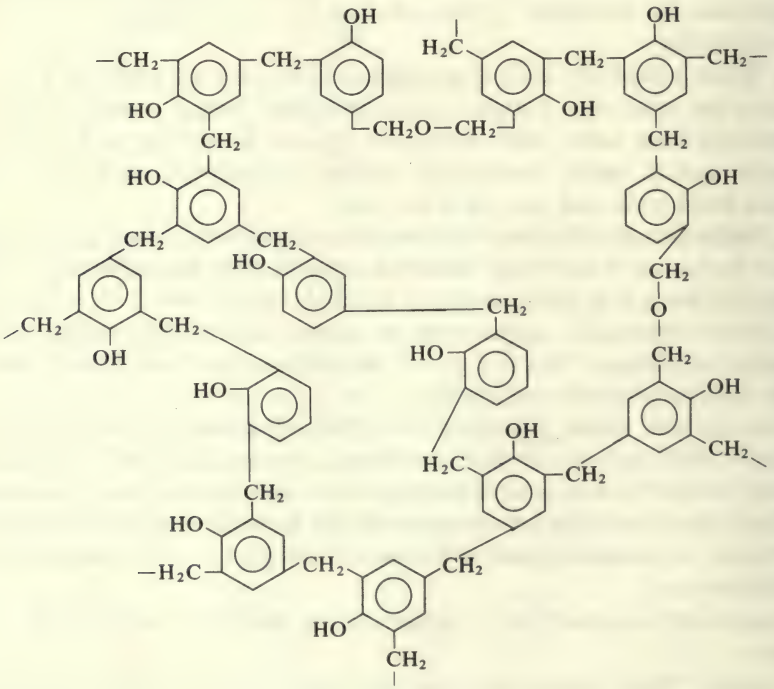


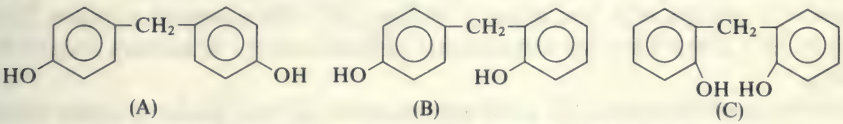
TABLE 17-1
Reaction Temperatures of Substituted Phenol Alcohols[a]

Para substituent	Temp. at which water is split off, °C	Temp. at which CH_2O is split off, °C
Methyl	135	145
Ethyl	130	150
Propyl	130	155
n-Butyl	130	150
t-Butyl	110	140
Phenyl	125	170
Cyclohexyl	130	180
Benzyl	125	170

[a] From Reference *1*.

17-2. Novolacs

A different product is actually produced by acid catalysis when the molar ratio of phenol to formaldehyde is greater than 1. The simplest type of novolac is dihydroxydiphenylmethane. Substitution may occur in either the *ortho* or *para* position. With unsubstituted phenol, three isomers are possible,



However, the only isomers that were ever isolated are (A) and (B).

Actually the above adducts were only isolated when large excesses of phenol were used in the reaction. When lower ratios of phenol to formaldehyde were used, chains were isolated which varied in size from 8 to 12 aromatic units (*9*). The addition apparently occurs in completely random manner. Here again, the number of possible isomers is very large.

The acid-catalyzed condensation of phenols and aldehydes can be a special case of the Friedel–Crafts reaction, with the aldehyde acting as the alkylating agent. The high nuclear reactivity of the phenol results in a great tendency for the reaction to proceed to the formation of diarylmethanes. The reaction can be illustrated as follows:

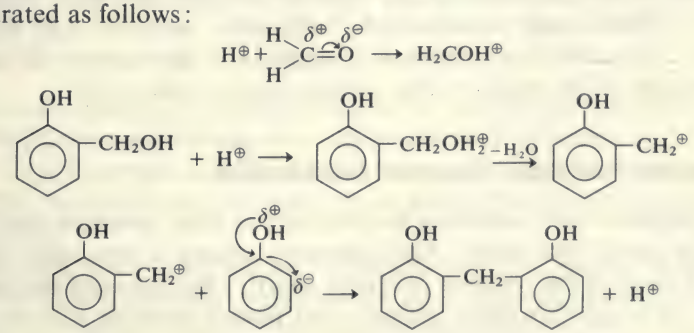


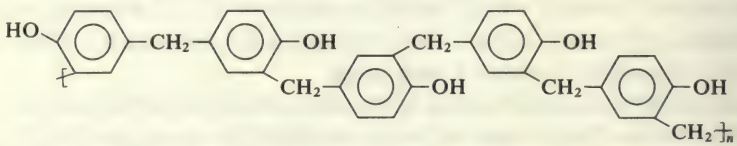
TABLE 17-2(*1*)

Moles HCHO/10 moles phenol	Mol. wt. of product	Type of resin formed
1	229	Dehydroxydipherylmethane
2	256	Novolac
3	291	Novolac
4	334	Novolac
5	371	Novolac
6	437	Novolac
7	638	Novolac
8	850	Novolac
9	1000	Novolac
12	?	Insoluble resin

Obviously, *para* isomers are formed just as readily and the product is a mixture of all the possible isomers.

The rate of the above shown electrophilic attack is proportional to the hydrogen ion concentration below pH 3.6, and the rate of the reaction is fast. The polymer structure that results is quite linear, with the actual concentration of methylol groups very low, about 0 to 5 per 100 of the phenol residues. This appears true (*24*) even with trifunctional phenols, where branching should be possible.

Martin comments that it is generally accepted (*2*) that acidic catalysts favor formation of *p,p'* linkages, although *o,p'* and *o,o'* linkages may also form. A highly idealized picture of a novolac molecule can, therefore, be shown as follows:



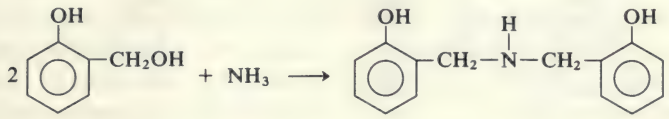
It should be remembered that this linear, fusible, and soluble polymer is only attained when the reactions are carried out with less than equimolar quantities of phenol and formaldehyde. Otherwise, insoluble and infusible resins result. The ratio of formaldehyde to phenol will also control the average molecular weight of the product. This is illustrated in Table 17-2.

17-3. Ammonia- and Amine-Catalyzed Condensations

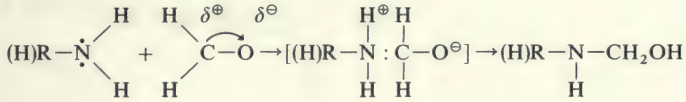
Resoles prepared with ammonia as catalysts are more complex than those formed with metal hydroxides. Also, ammonia causes a very rapid loss of solubility in water of the reaction products, shortly after the condensation has started (*2*). Although this might indicate that phenol alcohols will not form,

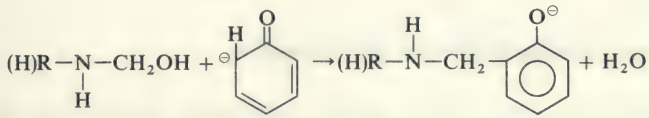
actually phenol alcohols and dialcohols were found present among ammonia-catalyzed condensation products (*25,26*).

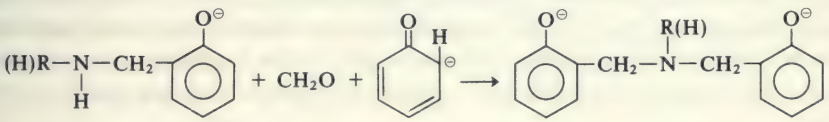
Paal and Senninger (*4*) were the first to demonstrate that when saligenin is heated with ammonia a dibenzylamine can be isolated,



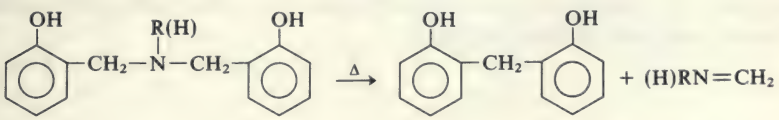
The mechanism by which ammonia (or amine) enters the reaction to become part of a bridged structure can be shown as follows:







The above shows the condensation to be a special case of the Mannich reaction. Further heating of the condensate will cause elimination of a mole of formaldehyde and ammonia (or amine) with the accompanying methylene bridge formation,

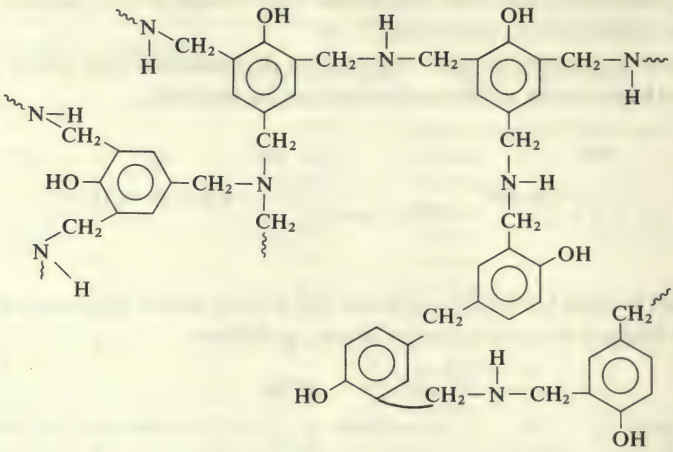


The amine-catalyzed condensations can be summarized as follows:

1. Additions and condensations occur almost simultaneously.
2. CH_2OH groups are present to the extent of 15–30 per 100 phenol residues.
3. The structures are branched, the degree of branching depending on the amine used.

Generally, resins catalyzed with ammonia have much higher melting points, and presumably molecular weights, than those catalyzed with caustic.

One can, therefore, picture the ammonia-catalyzed resoles as follows:

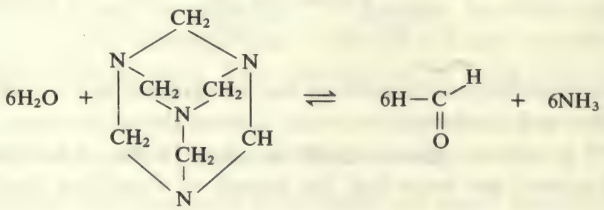


17-4. Cross-Linking Reactions of Phenoplasts

The phenolic resins convert rapidly and easily to well-knit, highly cross-linked products, as already stated. The commercial phenolic resins are either prepared as "one-stage" resins, or resoles that contain all the necessary attributes for the final hardening process, or "two-stage" resins, novolacs, which, prepared with a deficiency of formaldehyde, require addition of a curing agent for cross-link.

One-stage condensation of resoles is usually carried to the B stage. The reaction is then stopped and pH often adjusted. The cross-linking or curing to the C stage can then be achieved by further application of heat and also by addition of acidic reagents.

The cure of the novolacs is usually achieved by addition of hexamethylenetetramine, or sometimes paraformaldehyde. The hexamethylenetetramine is, of course, a source of formaldehyde,

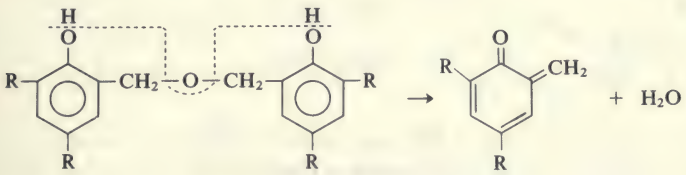


In the preparation of commercial resols, mixtures of trifunctional phenols, such as phenol and *m*-cresol, or phenol and resorcinol, are often used. Sometimes mixtures of tri- and tetrafunctional phenols (such as bisphenoles) are employed.

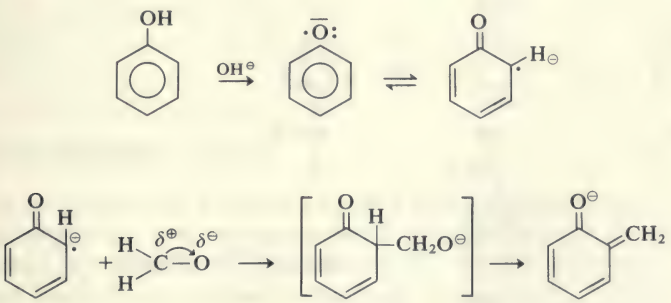
And the molar ratio of formaldehyde to phenol must exceed 1 to attain a thermoset material. This possibility of cure at ratios of formaldehyde to phenol greater than 1 appears to reach a maximum at a 1.5:1 ratio, and this, of course, is the reason this ratio is usually preferred (*2*).

For the novolacs to be capable of cross-linking in a "two-stage" resin, the phenols must have a functionality greater than 2. Sufficient quantity of the cross-linking agent must be added to attain an adequate number of cross-links. The total number of cross-links per phenol nucleus should be greater than 1:1 and to yield optimum results should approach the 1.5:1 ratio of the "one-stage" resins.

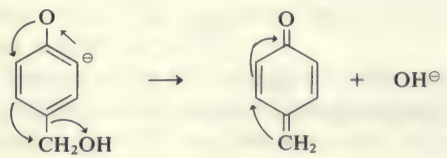
During the process of heat-hardening of phenolic resins, considerable darkening occurs. This was shown to be due to formation of quinone methides at higher temperatures,



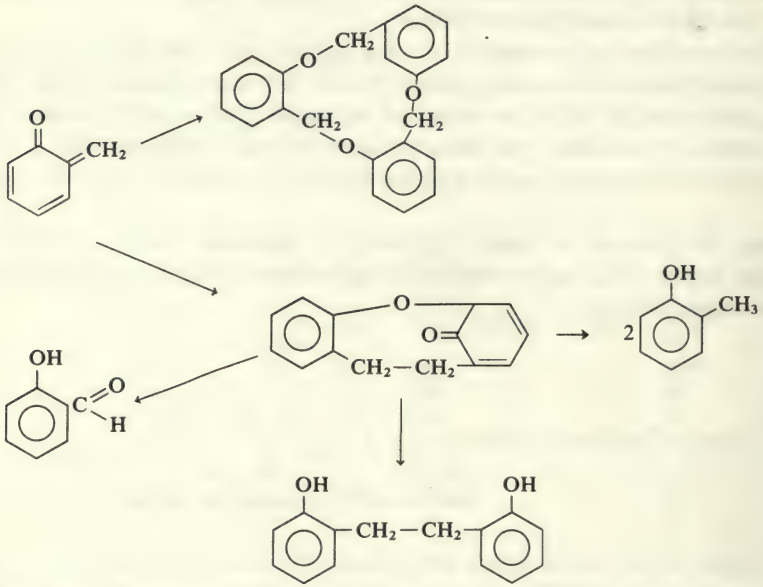
Freeman and Louis (*27*) postulated the mechanism of quinone methide formation through a direct condensation of phenol and formaldehyde at elevated temperatures,



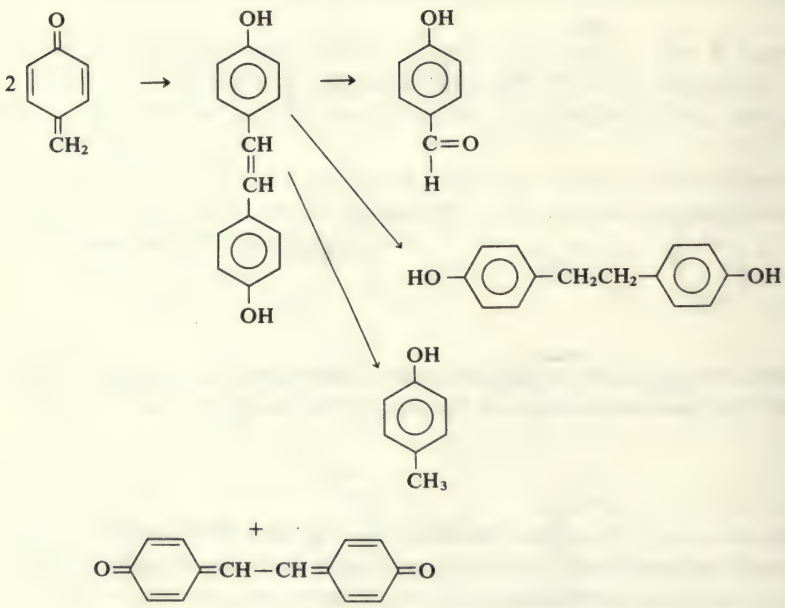
As shown, the migration of electron pairs leads to the formation of a quinone methide. The same migration can happen in the *para* position,



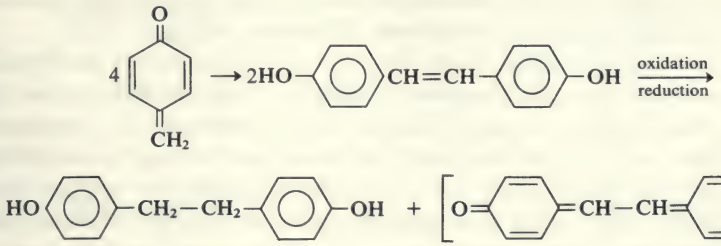
The quinone methide, being a very reactive molecule, can undergo a number of reactions.



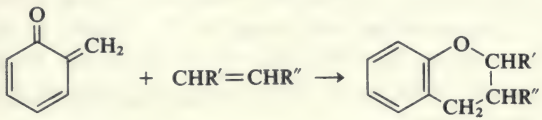
For the *para* methide,



von Euler and de Kispeczy (*28*) suggested that the paramethides lead to stilbenes,

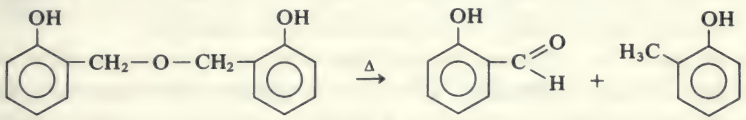


Furthermore, if olefins are present in the reaction mixture, the quinone methides can condense with them to form chromane rings (*29*),



Actually, phenol alcohols will also undergo this reaction with unsaturated compounds yielding benzopyrans. Or the alcohol might undergo the methide formation as an intermediate step in this reaction (*30*).

Hultzsch has also demonstrated (*31*) that thermal decomposition of dibenzyl ethers can lead to formation of aldehydes and methyl groups,



17-5. Acid Hardening of Resins

Resoles prepared with a molar excess of formaldehyde (more than 1 mole of formaldehyde per mole of phenol) can be cured rapidly at relatively low temperatures by addition of acids. Hydrochloric and phosphoric acids are often used, sometimes dissolved in glycerine or in a glycol. *p*-Toluenesulfonic acid and phenolsulfonic acid are also used for acid hardening. The reaction rate is proportional to the concentration of hydrogen ions (*31,32*). The reactions that take place are believed to be similar to those which occur in novolac formation, mostly leading to methylene bridges, unless the quantity of acid is small and the resol has a high amount of methylol groups. Then dibenzyl ethers were thought to form as well (*2*).

Resoles usually contain some free phenol as well as phenol alcohol. When acid is added, the reaction of formation diphenolmethane is very exothermic and can even be violent (*33–35*). One can now draw a general scheme for the

condensation reactions of phenol and formaldehyde. Such a scheme is shown in Figure 17-1. This scheme does not show any reaction intermediates or the composition of the products. One might also perhaps picture the reaction of phenol alcohols to proceed in the manner illustrated in Figure 17-2.

De Boer (*36*) calculated that if all the primary valence bonds are formed in the heat-hardened resin, the theoretical strength should be 4000 kg per mm^2. Actually, it was found to be only 8 kg per mm^2. Houwink (*37*) proposed his "Lockerstellen theory," which suggests that theoretical strength is not obtained because of flaws in the polymer. This is because all methylene bridges that are possible actually do not form, as all phenolic nuclei do not lie in the same plane. The unbridged gaps have a weakening effect. Presence of occluded reaction materials and by-products, such as water, cause further weakening.

A phenolic novolac, a tangled mixture of irregular compounds, has an average molecular weight of 500 to 600. When the resin is melted, the molecules will alter their configurations according to the degree of rotational freedom they possess. On cooling the resin may either freeze into numerous configurations and/or crystallize, although here it may be hindered due to the extreme complexity of the mixture.

The effect of rigidity caused by lack of rotational freedom might be signified by the fact that brittleness of phenolic resins increases in the order phenol, *m*-cresol, and 3,5-xylenol.

Megason concluded (*4*) from examining various possible configurations of novolac chains that on the grounds of probability a completely cross-linked phenolic structure is extremely unlikely. This should be true for C stage resols or for novolacs cross-linked with hexamethylenetetramine.

Over the last 10 to 15 years, chemical methods have been applied to establish the quantity of hydroxymethyl (*38*) and ether-bridge (*39*) groups in phenolic resins and also to learn as much as possible about the structures of the condensates. Infrared spectroscopy has shed some light on the structure by allowing

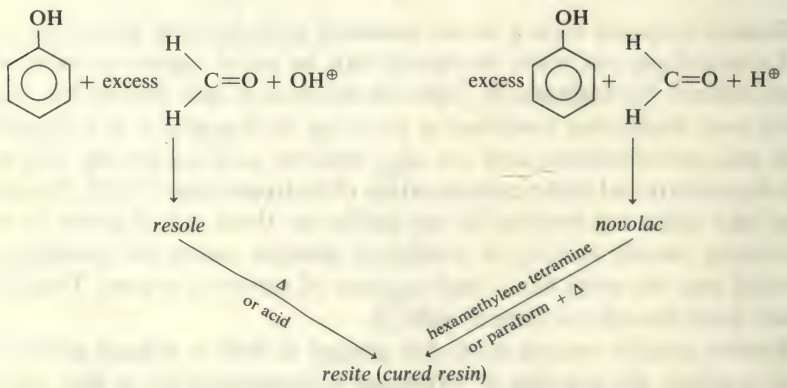


Figure 17-1. Reactions of phenol and formaldehyde. (From Reference *1*.)

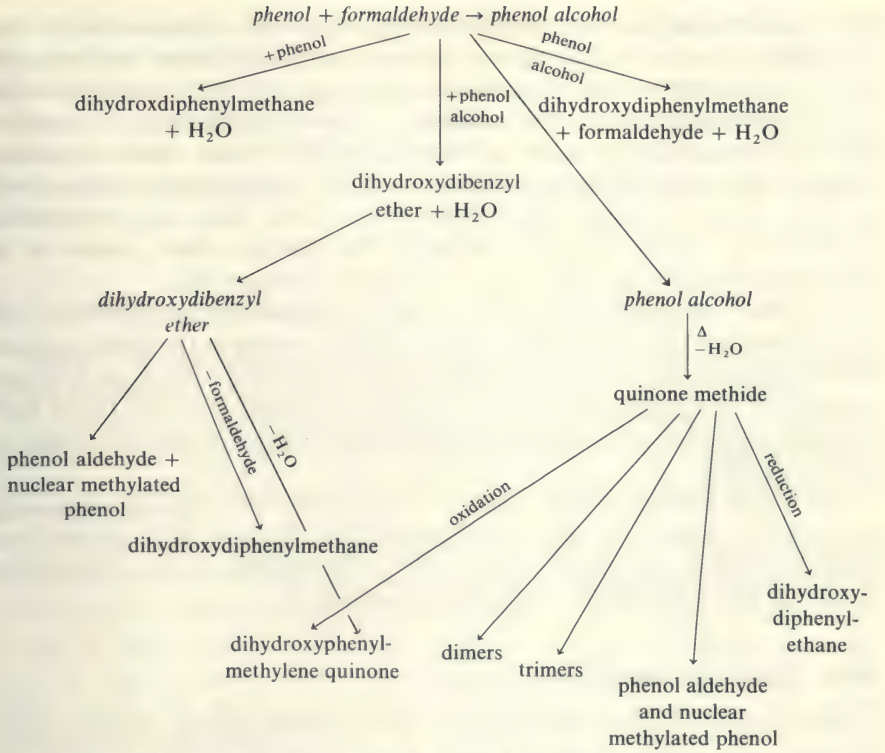


Figure 17-2. Reaction of phenol alcohols. (From References *1* and *4*.)

detection of hydroxymethyl groups (*40*) and phenolic rings (*40–42*). Infrared spectroscopy was also used to obtain a qualitative picture of the structure of the cross-linked and, therefore, insoluble polymers (*43*). Paper chromatography was found useful for studying resins in the early stages of their reaction sequences (*18,44*).

Hirst and co-workers (*45*) applied PMR spectroscopy to soluble novolac prepolymers to obtain direct measurements on the relative amounts of methylene bridges located at various positions on the phenolic rings.

Szymanski and Bluemle (*46*) demonstrated that arsenic trichloride is a useful solvent for NMR studies on heat-stable phenolic resins, both novolacs and resols. The last were prepared from alkyl-substituted phenols. This allowed them to obtain the molecular weights from NMR data. They demonstrated by this technique that a typical commercial novolac has an average molecular weight of 500–600, with fractions ranging all the way from 200 to nearly 1300. A molecular weight of 500–600 constitutes about five phenolic nuclei.

Woodbrey and co-workers (*47*) have made a further significant inroad into our understanding of the complex structure of soluble phenolic resins, also with the aid of PMR studies. They demonstrated that the novolacs contained

methylene-bridged phenolic nuclei only. The structures of the resoles fell into three different general types. Some contained methylene bridges and hydroxymethyl functionalities only. In addition to these groups, most resoles contained benzyl-type hemiformals. The presence of hemiformals tends to support Walker's suggestion on reaction mechanisms (*10*). A few resoles contained dibenzyl ether–type bridges, methylene bridges, hydroxymethyl groups, and, in some instances, benzyl-type hemiformals as well. They were not able to establish the relative quantities of either the dibenzyl ether groups or the hydroxymethyl groups, owing to the overlap of chemical shifts.

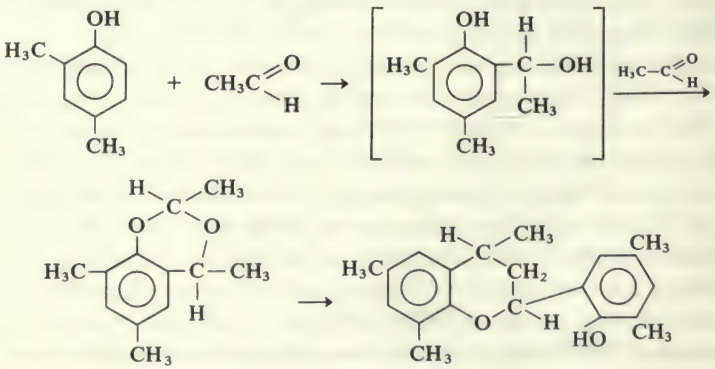
The PMR spectra (*47*) also showed that reaction at the *para* positions take place about five times faster under acidic conditions than at the *ortho* positions. With the resoles, on the other hand, apparently the *ortho* positions are hydroxymethylated much faster than the *para* positions. Also, reactions under basic conditions lead to *p,p'* condensations much faster than *o,o'*, and *o,p'* condensations combined.

The benzyl hemiformals were found to be quite stable, although apparently less stable at higher pH and temperatures. The fact that their presence was established sheds significant light on our understanding of the condensation of phenol and formaldehyde under basic conditions.

17-6. Reactions with Higher Aldehydes

Higher aldehydes, like formaldehyde, will react with phenols in the presence of Lewis acids and undergo the Friedel–Crafts reaction. To form a dihydroxydiphenylalkane one must control both the reaction temperature and the catalyst concentration or side reactions will take place.

Acetaldehyde follows formaldehyde in its reactivity toward phenol. This reactivity decreases with increase in the size of the aldehyde. Alder *et al.* (*48*) reported forming dehydroxyditolylethane from acetaldehyde and *p*-cresol. Substitution of 2,4-dimethylphenol for *p*-cresol led to a benzodioxan in benzene in the presence of HCl. Strong alkali or acid led to a chroman, which presumably formed via dimerization of a vinylphenol intermediate,



All the saturated aldehydes up to heptaldehyde were reported to form dihydroxydiphenyl alkanes with a variety of phenols under acidic conditions (*49,50*). Condensation of chloral with various phenols was also reported (*51*).

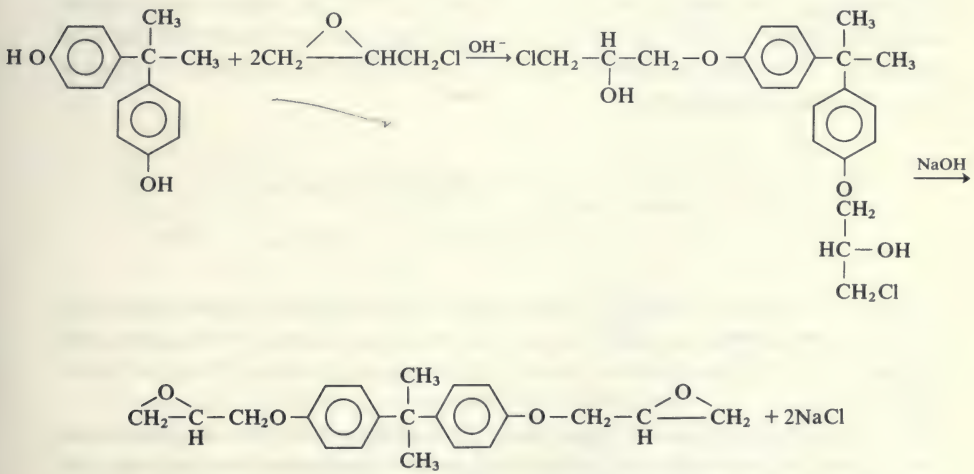
Reactions of phenols with certain higher aldehydes also appear possible in some cases under basic conditions (*2*). The products appear identical to those formed with acidic catalysts, although the mechanism of the reaction might be different.

17-7. Reactions with Ketones

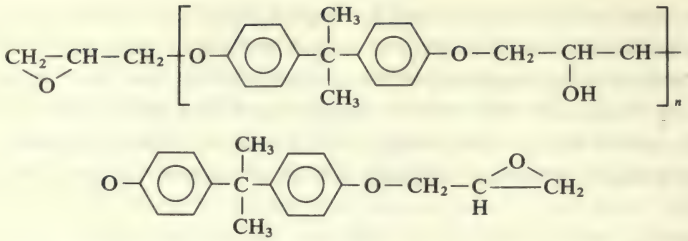
Phenols will also undergo condensation with ketones when acid-catalyzed. Lower temperatures (25–60°C) are recommended to avoid side reactions.

In this reaction with ketones, phenols show a greater tendency to stop at a bisphenol stage than they do with aldehydes, where a large excess of phenol would be required. But, as a result of this, high-molecular-weight products are not formed readily.

The bisphenols have considerable utility in polymer technology, however, as starting materials for other condensation polymers, such as preparation of polyesters, particularly polycarbonates, and also in the preparation of monomers for use in epoxy resins, such as diglycidyl ethers. One bisphenol commonly used for this purpose commercially is 2,2′-bis(4-hydroxyphenyl) propane (Bisphenol A). The diphenol is reacted with 2 moles of epichlorohydrin in the presence of a basic catalyst.

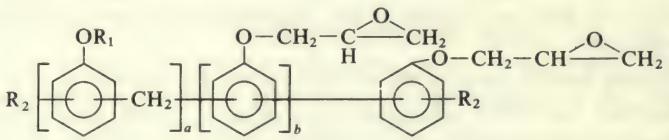


When the reaction of epichlorohydrin with the diphenol is catalyzed with sodium hydroxide, higher homologs tend to form, with the final product containing polymeric species,



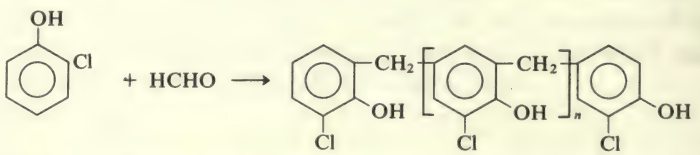
The products tend to be less colored and contain less polymeric species if sodium hydroxide is replaced by zinc chloride and the ring closure carried out with $Na_2SiO_3 \cdot 5H_2O$. A very light colored material can be obtained by this procedure, with the monomer being pure enough to crystallize.

Low-molecular-weight novolacs can be used in place of bisphenol to form glycydol ethers, and this is also done commercially with reasonable success,



17-8. Higher-Molecular-Weight Linear Polymers

A series of linear, relatively high molecular weight polymers were prepared by Burke and co-workers (*42,52–55*) when difunctional phenols were condensed with a slight excess of formaldehyde in the presence of acidic catalysts. Thus, *o*-chlorophenol condensed with formaldehyde at 150°C in a closed system when bis(2-ethoxyethyl) ether was used as the solvent and *p*-toluenesulfonic acid as catalyst. The chlorophenol was found to be linked by methylene bridges at the *ortho* and *para* positions:



The above polymer could be dehalogenated by sodium in liquid ammonia. The resulting polymer tended to cross-link much more slowly by reaction with hexamethylene-tetramine than all-*ortho-ortho* isomer prepared from *p*-chlorophenol.

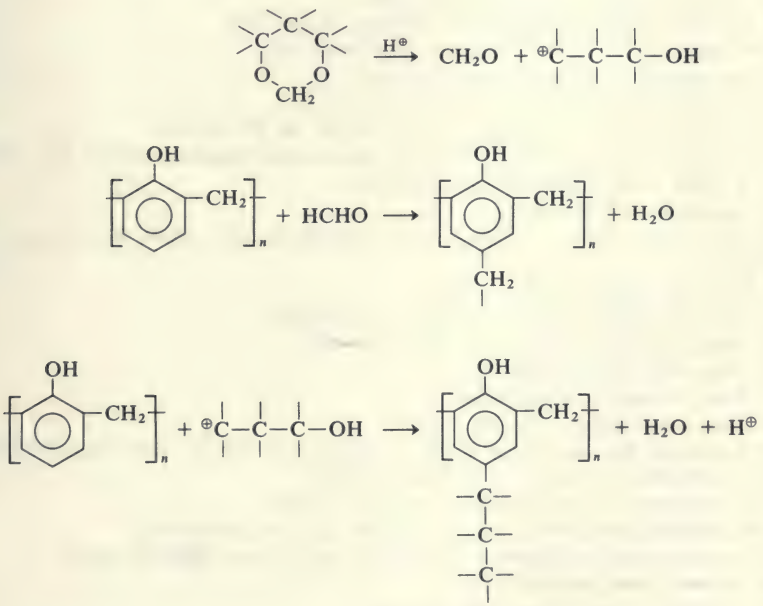
A variation of this was achieved when 2,6-bis(chloromethyl)-4-chlorophenol was reacted with *p*-cresol to first form 2,6-bis-(2-hydroxy-5-methylbenzyl)-4-chlorophenol. This trimer was then condensed with formaldehyde in the presence of *p*-cresol to yield linear *p*-cresol-*p*-chlorophenol-formaldehyde polymers having 1, 2, and 4 *p*-chloro substituents per 12 phenolic residues. Dehalogenation could also be achieved with sodium in liquid ammonia. In

addition, they also carried out nitrosation of the *o,o*-linked linear phenol-formaldehyde polymer in aqueous *N,N*-dimethylformanide to yield *p*-benzaquinone monoxime repeating units.

It is interesting that as a result of this work, Burke and Higginbottom (*55*) found that the physical and chemical properties of the polymeric isomers were strikingly different. The approach offers considerable promise for preparation of high-molecular-weight polymers of phenol-formaldehyde which have sterically controlled arrangements.

17-9. Curing Phenolic Resins with Formals

Heslinga and Schors (*56*) found that phenolic resins can be cured by cyclic formals in the presence of strong acids. Thus instead of using hexamethylenetetramime or paraformaldehyde, a novolac can be combined with a cyclic formal and an acid. Application of heat caused decomposition of the formal and cross-linking of the novolacs,



The formal is, therefore, another source of formaldehyde, like hexamethylenetetramine, provided it was prepared from a glycol and formaldehyde. Other formals have also been used over a considerable period of time for blends with phenolic resins. This is particularly common when the resins are used for coating purposes. Then poly(vinyl butyral) or poly(vinyl formal) may be combined with the phenolic resin. Very little concrete proof has been presented, however, as to the correactivity of the two molecular species, except that it is

reasonable to expect the acetals to be sources of aldehydes at elevated temperatures.

Cohen *et al.* (*57*) studied the chemical interaction of poly(vinyl formal) with phenolic resins. They concluded that under the influence of phosphoric acid catalyst, the polymeric acetal undergoes cross-linking at 175°C in 30 minutes. When phenolic resins are present the poly(vinyl formals) will cross-link through free hydroxyl groups with phenolic methylol groups at 150°C in 30 minutes.

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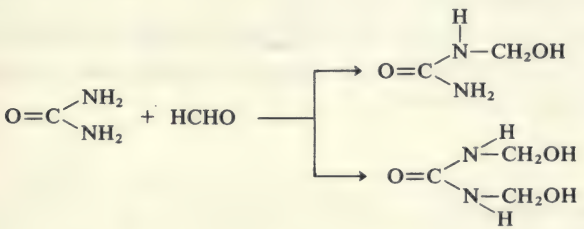
Aminoplasts

18

The term *aminoplasts* applies to resinous condensation products of aldehydes with amines such as urea, melamine, guanidine, guanamine, and so on. Some chemistry of the more commonly known species of these resins will be discussed here. The most commonly used aldehyde is formaldehyde, although some higher aldehydes were investigated.

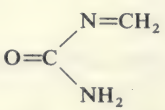
18-1. Urea-Formaldehyde Resins

Urea reacts with formaldehyde at pH 7.3–8.5 to yield mono- and diadducts,

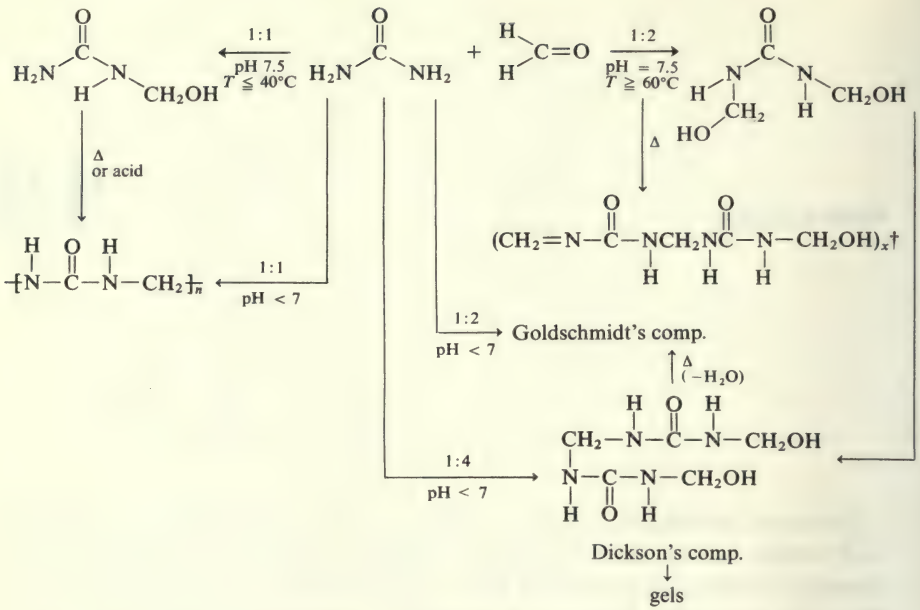


The mechanism of the condensation probably is a typical electrophilic attack by the aldehyde on the nucleophilic urea.

Significantly, methylene urea can be found among the reaction products,



The course of the reaction is actually dependent upon the ratios of the reactants used and the reaction temperature,



Usually the urea-formaldehyde condensation is carried out in three steps:

1. Initial condensation to form monomethylol urea at pH greater than 7.
2. Polymer-forming step (polycondensation) at pH less than 7.
3. Cross-linking of the polymer to form gels, also at pH less than 7.

Smythe (*1–3*) describes these steps as follows: Step 1 is a fast step which consumes 25% of formaldehyde. Step 2, on the other hand, is slow, but in this step 70% of formaldehyde is consumed.

In discussing the mechanism of the reaction, Smythe points out that we should think of aqueous formaldehyde as being an equilibrium of four compounds including a dimer and a trimer,

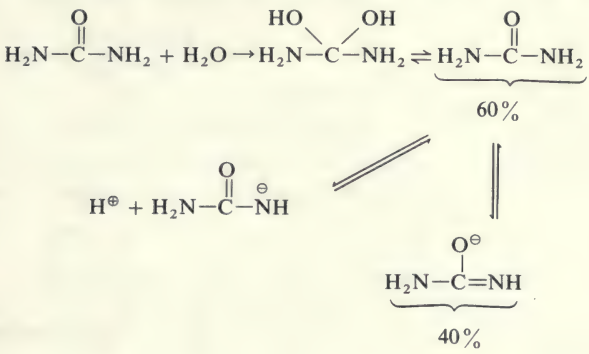
$$\underbrace{HCHO}_{49\%} \rightleftharpoons \underbrace{HOCH_2OH \rightleftharpoons HOCH_2{-}O{-}CH_2OH \rightleftharpoons HO{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}CH_2OH}_{51\%}$$

But when the molar concentration of formaldehyde in water drops to 0.5%, then it is mostly a hydrate,

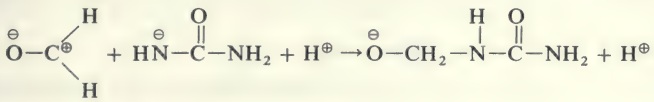
$$\underbrace{HCHO}_{2\%} \rightleftharpoons \underbrace{HOCH_2OH}_{98\%}$$

† The structure shown is one often pictured.

At the same time, aqueous urea can also be shown in this form,

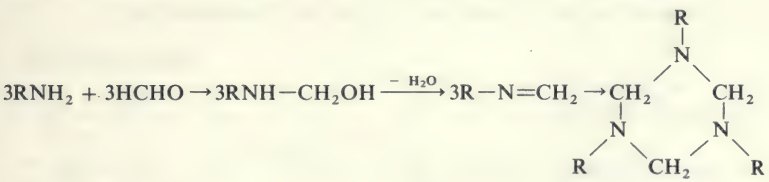


So Smythe (*1*) pictures the reaction mechanism of an electrophilic attack by formaldehyde on a nucleophilic urea in this manner:

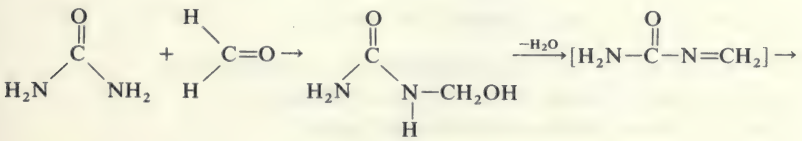


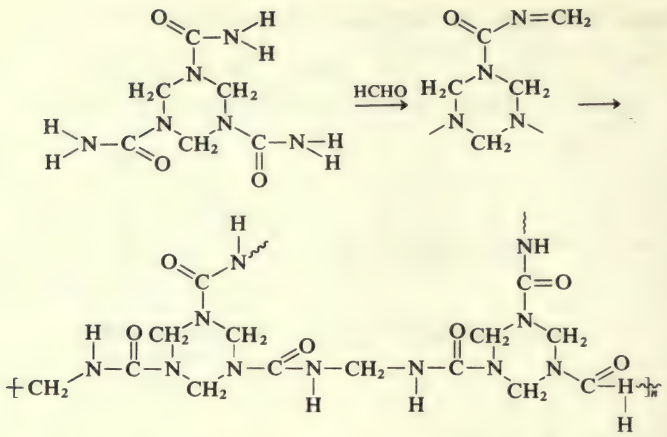
As the pH increases, the rate of formation of the reactive species increases.

Marvel and co-workers (*4*) originally speculated that the products of condensation might include ring structures, based on the assumption that urea is an amino amide. The amine should react with formaldehyde, forming a Schiff's base and then lead to a trimer with loss of water,

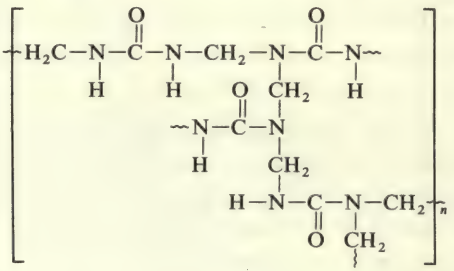


Free amide groups in the trimer can then react with formaldehyde to cross-link the polymer,





To form such a condensate, one would require a ratio of 1 : 1.5 moles of urea to formaldehyde. Such ratios are actually often used for forming these polymers. Evidence was presented (*5*), however, which indicates that the products are mostly noncyclic methylene ureas possessing linear and branched segments,



In such a study deJong and deJong (*5*) found the following kinetic relationships for intermediates in reactions of urea and formaldehyde:

	Rate constants
2-Monomethylol urea $\xrightarrow{k_1} p_1$	$k_1 = 0.85 \times 10^{-4}$
Monomethylol urea + urea $\xrightarrow{k_2} p_2$	$k_2 = 3.3 \times 10^{-4}$
2-Dimethylol urea $\xrightarrow{k_3} p_3$	$k_3 = 3 \times 10^{-6}$
Dimethylol urea + urea $\xrightarrow{k_4} p_4$	$k_4 = 2 \times 10^{-4}$
Monomethylol urea + Dimethylol urea $\xrightarrow{k_5} p_5$	$k_5 = 0.5 \times 10^{-4}$

Typical catalysts for urea-formaldehyde condensation are:

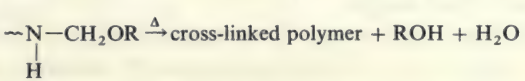
1. Acids: tartaric, oxalic, citric, benzoic, phthalic.
2. Acid liberators: ammonium silicofluoride.

Stabilizers are sometimes employed to prevent the methylol ureas from cross-linking prematurely. Among those commonly used are:

1. Hexamethylenetetramine.
2. Ammonium carbonate.
3. Phenyl silicate.

Modification of urea-formaldehyde condensates is possible by carrying out etherification reactions with alcohols. This yields solubility in many nonpolar organic solvents, depending on the chain length of alcohol used,

Butanol is often used for this reaction. The ether links are heat-labile,



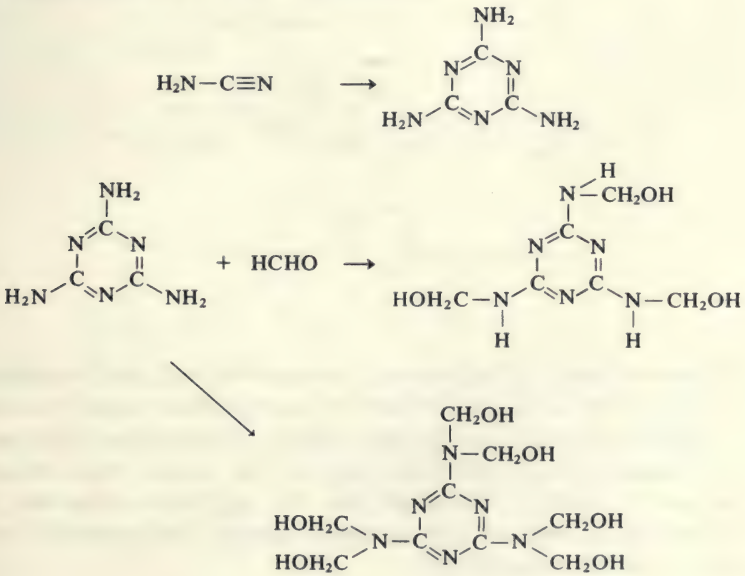
Reactions with alcohols higher than capryl are difficult to carry out.

The etherification of methylol groups has the added advantage of reducing the likelihood of gelation at moderate temperatures.

18-2. Melamine-Formaldehyde Resins

Melamine reacts with formaldehyde in much the same way as urea-forming products containing varying amounts of N-methylol substitution depending on the mole ratio of the reactants.

The amine itself is a trimer of cyanamide,



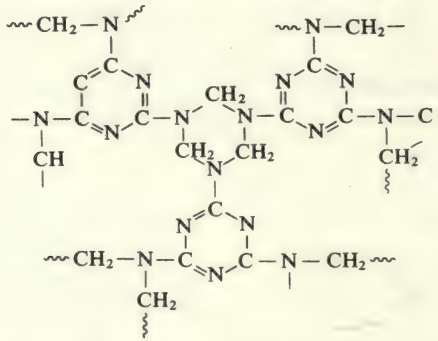
The properties of melamine-formaldehyde polymers are quite similar to those of urea-formaldehyde polymers, except that they exhibit greater moisture resistance and are harder.

Actually a variety of reaction products are possible from melamine and aldehydes. Some of these products can be isolated in crystalline form, although the tendency is to form condensation polymers. The most commonly studied reactions, however, are with formaldehyde (*6–8*).

Products from condensation of melamine-formaldehyde depend upon pH, mole ratio, and temperature. In neutral solutions the reaction proceeds rapidly beyond the methylol stage. Of the methylol series, the dimethylol derivative is the lowest member isolated so far (*6–8*). Although the reaction products are complex mixtures of methylol derivatives, tri-, and hexamethylols can be produced in a relatively pure state.

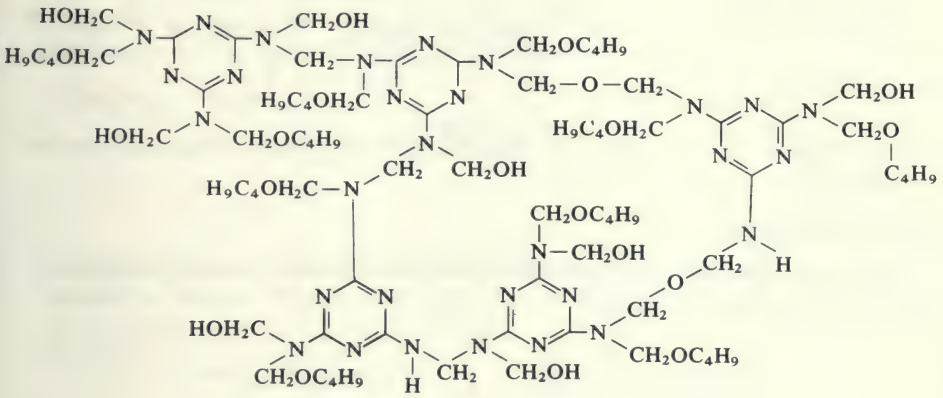
When the reaction is conducted on the alkaline side, a resinous syrup forms which tends to continue to polymerize and finally becomes insoluble. Wohnsiedler (*9*) found that useful resinous materials are prepared in the pH range 4 to 6. These products can be polymerized rapidly to form resinous amorphous polymers.

The structure of the final polymer might presumably be the result of water elimination between N-methylol groups and the remaining —NH— groups. Condensation of hexamethylol melamine may involve either formation of ether groups from the N-methylol groups, or condensation through elimination of some formaldehyde. One might perhaps picture formation of cyclic structures as follows:



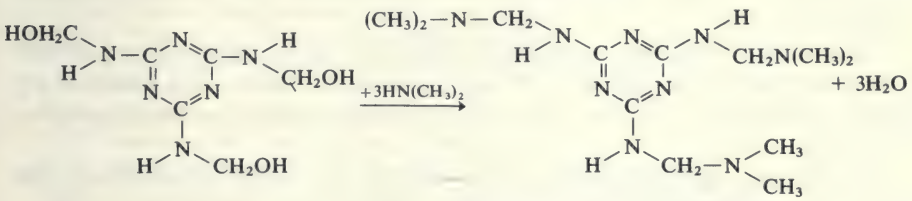
Etherification of methylol melamines can be carried out just as readily as of methylol ureas to form a range of resinous products. Those formed with methyl and ethyl alcohol are water- and alcohol-soluble, whereas those obtained with butanol are soluble in aromatic hydrocarbons. The reaction with alcohol can be carried out at slightly acidic conditions. The product is a function of the ratio of formaldehyde, the type and amount of catalyst, the degree of etherification, the time, and the temperature.

A typical butylated melamine-formaldehyde resin of low molecular weight can be represented as follows:

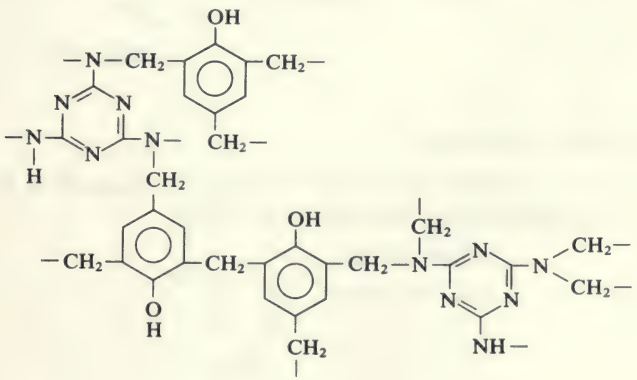


The molecular weight of this compound is 1510.

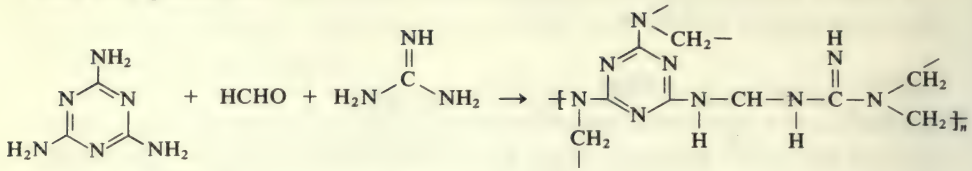
Methylol melamines have been treated with mercaptans, such as benzothiazol, to give *s*-substituted methylol melamines. Amines have also been combined with melamine and formaldehyde to yield aminomethyl derivatives. Secondary amines appear to yield better reactions than the primary ones.



It is possible to condense melamine resins with phenolic,



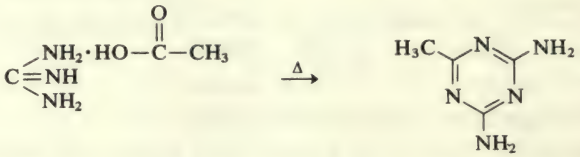
and with guanidine,



Condensations with urea are also possible, yielding resins similar in structure to the above.

18-3. Guanamines

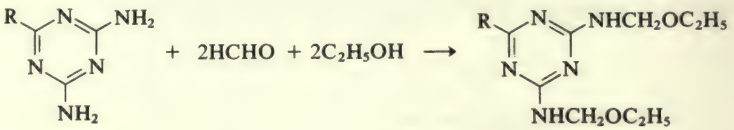
The term *guanamine* was originated by Nencki (*10*), who formed the compound by fusion of guanidine acetate,



Guanamines will condense with formaldehyde in aqueous solution to yield a variety of derivatives (*11–13*) which are methylol compounds. At elevated temperatures as well as at room temperatures and proper pH of the solution, the reaction proceeds rapidly, first forming hydrophilic and then hydrophobic resins.

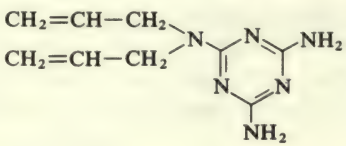
Reactions of guanamines with higher aldehydes in the same manner as with formaldehyde appears possible. At least one such instance was reported by Keller and Hansen (*14*), who carried out a reaction with trimethylol acetaldehyde.

Just like urea and melamine, guanamines will react with formaldehyde and alcohols in the presence of acids to form alkoxymethyl guanamines (*12,13*),

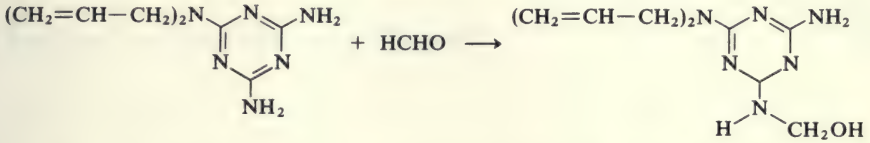


18-4. N,N′-Diallyl Melamine

This monomer is a dialkyl derivative of melamine designed to have greater functionality and applicability than melamine itself,



The monomer may be addition-polymerized alone or with a variety of other monomers by free-radical mechanism to form curable resins. It also forms condensation compounds with formaldehyde quite readily. The monomethylol derivative can even form with 1 mole of formaldehyde in neutral aqueous solution without the aid of catalysts (*15*),



When 2 or more moles of formaldehyde are used and the condensation carried out under alkaline conditions, clear hydrophobic products are reported (*15*). Heating will thermoset this material.

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Ladder and Semiladder Polymers 19

19-1. Polymers with Rigid Backbones

Linear polymers that contain only single bonds or primarily single bonds between the atoms in the polymer backbones allow rapid conformational changes. If these chains are regular, and/or if there are considerable intermolecular forces, the materials are crystallizable, relatively high melting, rigid, and difficult to dissolve. But if the chains are irregularly built, they are more likely to be amorphous, soft, and rubbery.

Ether and imine bonds or double bonds in the *cis* form tend to reduce the energy barrier for rotation of the adjacent bonds and thereby tend to "soften" the chains in the sense that the polymers become less rigid, more rubbery, and more easily soluble than corresponding chains composed of consecutive carbon-carbon bonds. This is particularly true if the "plasticizing" bonds are irregularly distributed along the length of the chains so that they not only do not favor, but even inhibit, crystallization (Chapter 2).

Cyclic structures occurring in the backbone of polymer chains exhibit an even greater effect and actually drastically inhibit conformational changes and lead to difficult or slow crystallization. This effect can become so pronounced that under most practical conditions, the polymer will remain amorphous.

Polymers to be useful as fibers, films, coatings, and adhesives must possess a combination of properties: (1) high modules of rigidity; (2) high softening and melting point; (3) high tensile strength; (4) high elongation to break; (5) resistance to swelling by solvents, often even at elevated temperatures; (6) and high resistance to deterioration from heat, radiation, and chemical attack. These properties can be achieved in three ways: (1) by crystallization, or (2) by cross-linking, or (3) by the inflexibility of chain molecules.

Crystallization of polymers means the formation of domains or regions of high lateral order in an otherwise amorphous material, domains where spaghetti-like tangled molecules line up with each other for discrete distances and pack close together in a manner often compared to matchsticks in a bundle. The effect of this can be illustrated by typical examples.

Linear polyethylene, a completely nonpolar material with weak interchain bonding, is rigid, high-melting (130°C), strong, tough, abrasion-resistant, and insoluble in anything at room temperature (because it possesses a strong tendency to crystallize). The same is true of isotactic polypropylene (m.p. 170°C) and of isotactic polystyrene (m.p. 230°C) (see Chapter 2).

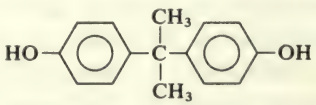
The behavior of natural rubber also illustrates the influence of crystallization. In the unstretched form, it is very soft (modulus around 20 psi), melts at low temperature, and dissolves very easily in many organic solvents. As samples of rubber are stretched, however, their kinked chain molecules straighten out and become parallel, and establish firm lateral bonding. On maximum stretching at 600–700% elongation, the extended rubber acquires a modulus of 20,000 psi. At this stage the polymer will swell only moderately in organic solvents, and will soften only at high temperatures. Elongation of rubber and incidentally of many synthetic elastomers with regular chain structures evidently confers rigidity by forming elastomer crystals, which act as natural reinforcing fillers.

When the melting point of the crystalline domain is below the ambient temperature, elongated samples will have a tendency to contract and, as a consequence, the material will be an elastomer. If, however, their melting point is substantially above the temperature level, they will have the character of strong rigid fibers. Thus poly(cis-butadiene) and poly(cis-isoprene) are rubbers (their elongated samples contract) because the melting point of their crystalline domains is around 20°C, whereas nylon 6-6 is a fiber, because its T_m is 260°C.

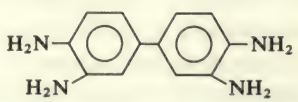
What happens is that in a crystalline system the rigidity is the result of many regularly spaced lateral bonds between the oriented chains, and, although each of these bonds is weak, the ultimate effect comes from their large numbers and their regularity. In a cross-linked system, the bonds between the flexible chains are strong but strictly localized, for in their entirety they are randomly arranged in the system. As a result, crystallization is a reversible phenomenon, whereas cross-linking is irreversible.

Crystallization is also a physical effect that takes place at all temperatures and is strongly influenced by physical processes, such as orientation and swelling. It can be likened to physical means of cross-linking. True cross-linking, on the other hand, is a chemical phenomenon that requires certain chemical conditions. But it is also possible to achieve this result in a third way, by starting with rigid monomeric units to form the backbones, such as:

Bisphenol:

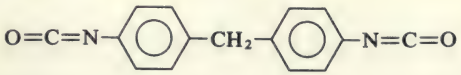


Tetraaminobiphenyl:



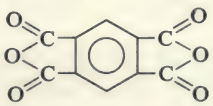
Terephthalic acid:

Methylene bisphenylisocyanate:



Paraphenylene diamine:

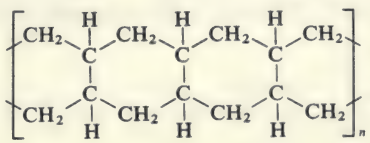
Pyromellitic dianhydride:



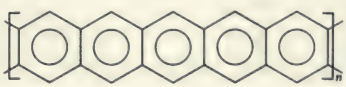
(and many others) and then synthesize a series of polymers from them which are substantially amorphous but very hard, high-melting, and solvent-resistant.

Examples of such polymers are polybenzimidazoles, polyimides, and polyphenyloxazoles. These polymers exhibit heat stabilities at temperatures sometimes up to 500°C for long periods of time, and often are completely insoluble in all organic solvents up to 300°C.

The above polymers are perhaps precursers or halfway points to the so-called *ladder polymers.* Actually an ideal ladder polymer would be one composed of two parallel chains of molecules and possessing regular cross-links. Such an imaginary ladder polymer might be one composed of fused cyclohexane rings,



It would be, perhaps, even more preferable to have a ladder polymer composed of fused aromatic rings to attain added bond strength from the resonance energy as well as rigidity from the planarity of the rings,

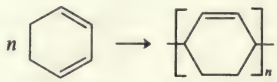


Degradation of such macromolecules would require simultaneous rupture of several bonds and, therefore, a great deal of energy.

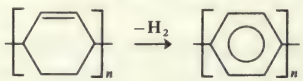
Nevertheless, considerable utility can be found in structures which are often called *semiladder polymers,* and possessing rigid rings in the backbones.

Such polycyclic polymers can be prepared by a variety of methods. Thus Berlin and co-workers (*1*) reported the formation of essentially a polyphenylene from 4,4′-biphenylylbisdiazonium salt which they reacted with cuprous compounds. Unfortunately, the reaction was not complete and there were azo links left in the backbone,

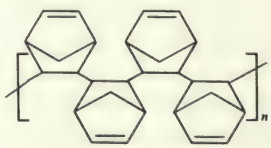
Stille (*2*) demonstrated that cyclohexadiene can be converted in a high yield to a linear polymer with the aid of Ziegler catalysts,



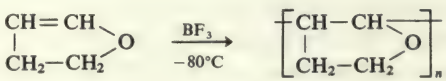
Marvel and Hartzell (*3*) carried this further, demonstrating that a polymer of 1,3-cyclohexadinene can be formed which has the molecular weight of 5000 to 10,000 with the softening point of 170–180°C and which is soluble in benzene. The macromolecules can be dehydrogenated with the aid of chloranil into polyphenylene, a black powder which does not melt in nitrogen atmosphere at temperatures as high as 530°C and can be maintained in air for 72 hours at 230–240°C without any changes,



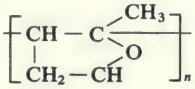
In a similar manner, bicyclo(2,2,1)-heptadiene can be polymerized by free-radical mechanisms or with the aid of ultraviolet light (*4*) to form a material that does not soften at 350°C although it decomposes at 400°C. The polymer is linear and amorphous,



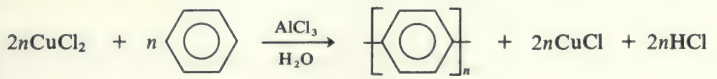
Barr and Rose (*5*) obtained linear polymers composed of heterocyclic rings by polymerizing dihydrofurans by means of cationic mechanism. The products were linear, high-molecular-weight structures with the softening temperature of 118°C,



When a 2-methyl group was present in the molecule, the softening temperature of the polymer was 245°C,

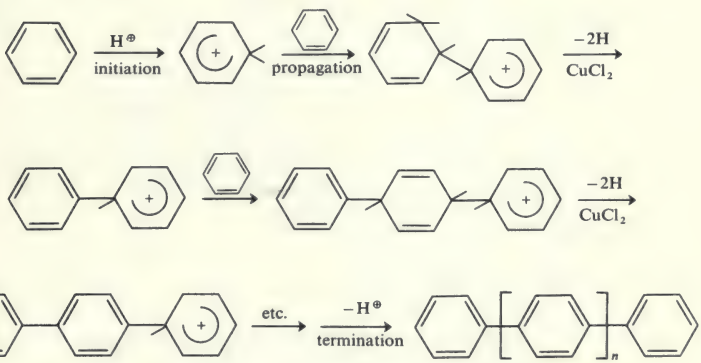


Because polyphenylene is potentially the ultimate in what might be considered as a semiladder polymer, another approach to its synthesis was investigated by Kovacic and Kyriakis (*6*), who polymerized benzene with the aid of Lewis acids-oxidants to form polyphenylenes. Cupric ions served as oxidizing agents.



Benzene was also found to polymerize under mild conditions on treatment with aluminum chloride–cupric chloride–water to a solid polymer. They assigned the following reaction sequence:

$$AlCl_3 + H_2O \rightleftharpoons H^{\oplus}AlCl_3(OH)^{\ominus}$$

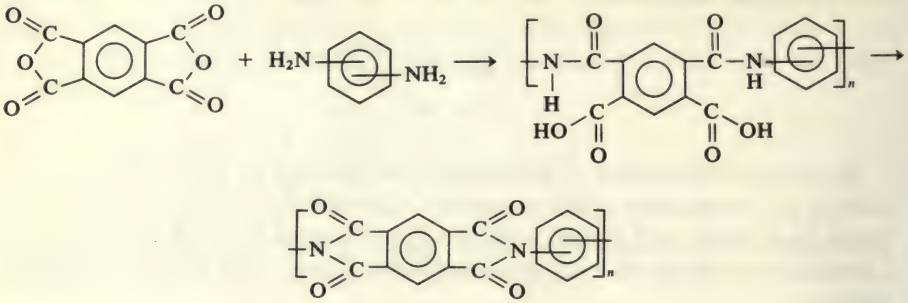


In a subsequent paper Kovacic and Lange (*7*) reported benzene polymerization with the aid of molebdenum pentachloride. The product was of low molecular weight and contained some chloro- and dichlorobenzene. A similar oxidative cationic mechanism to the one shown above was offered.

This reaction was studied further (*8–10*), with the conclusion that from among a large number of catalysts and oxidants examined, only those metal halides which possess high Lewis acid strength can be used as catalysts for polymerization of benzene to *p*-polyphenylene.

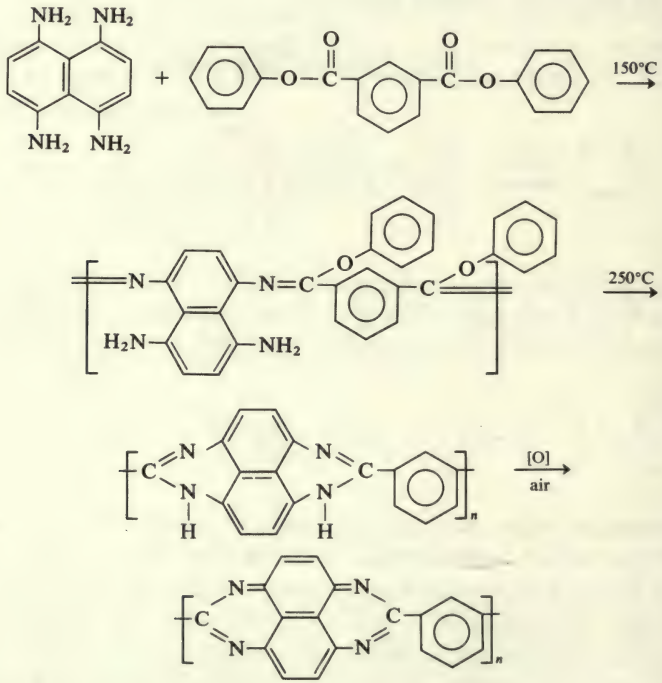
Many other attempts were also made to form semiladder polymers, but with heterocyclic rings in the backbones. Thus Sroog and co-workers (*11*) condensed

aromatic diamines with pyromellitic dianhydride to form



a polyimide

A closer step to formation of true ladder polymers was taken by Dawans and co-workers (*12*) when they attempted to form fully conjugated polymers based on tetraazopyrene. These compounds, however, are still, strictly speaking, semiladder structures:



In place of the isophthalic ester, terephthalic and 2,6-naphthalene dicarboxylic acid esters were also used. The esters could also be substituted with acid chlorides. Thermogravimetric analysis of the three resultant polymers showed stability in nitrogen to about 450–500°C with a weight loss less than 30% at

840°C. In air, however, these polymers lost weight rapidly at about 425°C. All the materials were black in color. ESR studies demonstrated some unpaired electrons in the macromolecules. In spite of the high degree of conjugation, they failed to conduct electric current. This suggests lack of complete aromaticity in the structure. Generally, polymers that have only aromatic structures as their recurring units should not degrade in vacuum or nitrogen atmosphere below 500°C and some even near 600°C. The degradation pattern of these polymers is shown in Figures 19-1 and 19-2.

The nature of the recurring unit does not seem to have very much influence on the temperature at which degradation would occur. On the other hand, there are some differences in the ease of oxidation of various aromatic structures and some differences in retention of physical properties at elevated temperatures.

After a number of studies Dawans and Marvel described (*13*) the formation of polymers in which aromatic rings are linked by imidazolone groups. This was achieved by carrying out a polycondensation of tetrafunctional reagents such as 3,3′-diaminobenzidine with pyromellitic anhydride. When 1,2,4,5-tetraminobenzene and 1,4,5,8-tetraaminonaphthalene were employed, true conjugated ladder structures were apparently obtained,

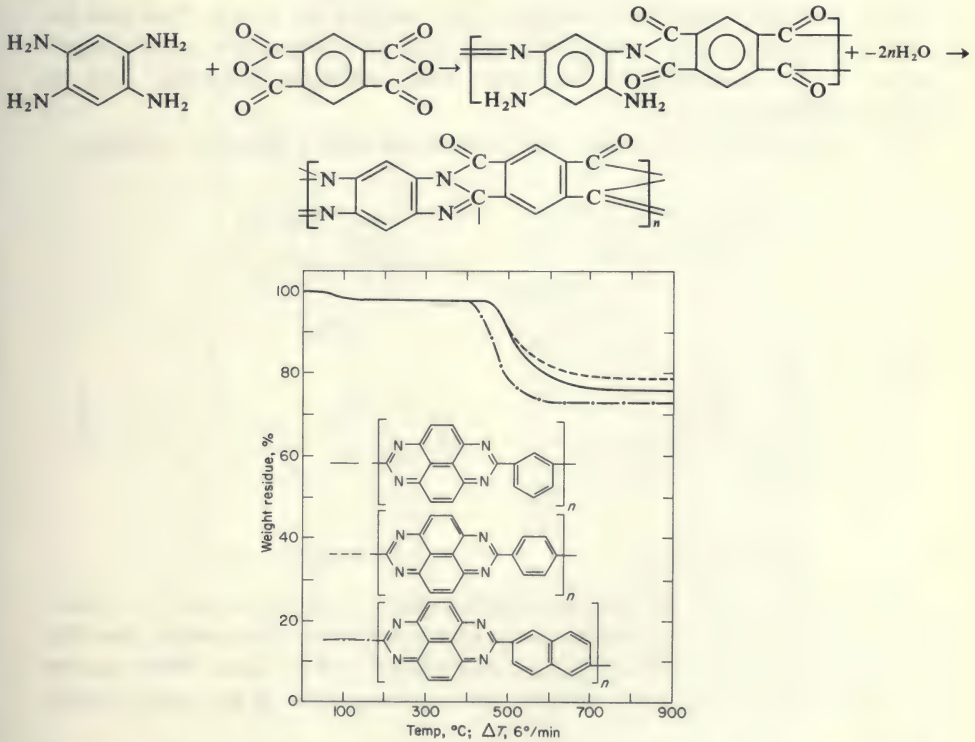


Figure 19-1. TGA in nitrogen. (From Reference *12*; courtesy of the *Journal of Polymer Science*.)

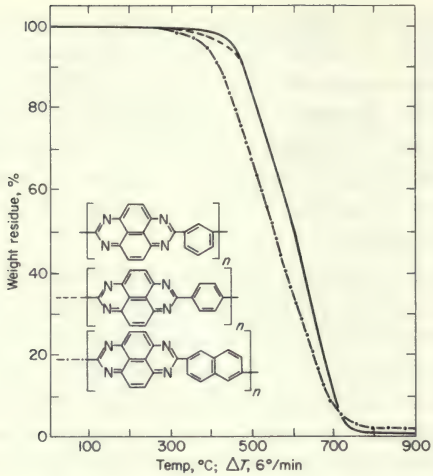
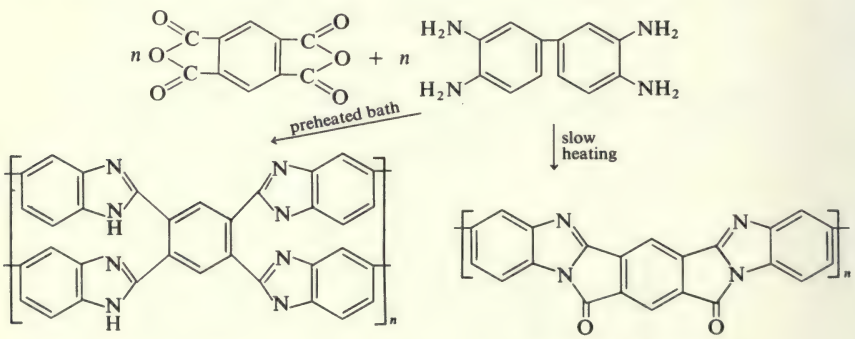


Figure 19-2. TGA in air. (From Reference *12*; courtesy of the *Journal of Polymer Science*.)

Study of model compounds indicated that varying the heating rate and the starting anhydro/amine molar ratio will lead to either *o*-phenylenebibenzimidazole or 1,2-benzoylbenzimidazole from phthalic anhydride and *o*-phenylenediamine.

This was applied (*13*) to melt polycondensates with a different tetramine,

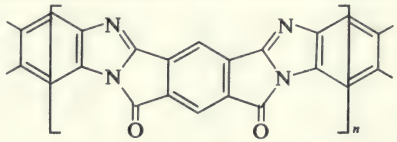
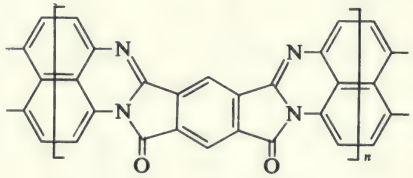


ladder structure *semiladder structure*

Marvel found that the polybenzimidazolones are colored powders which melted above 400°C, and which were soluble in dimethyl formamide, dimethyl acetamide, dimethyl sulfoxide, and concentrated sulfuric acid. When ladder polymers were subsequently formed, they were insoluble in the usual organic solvents.

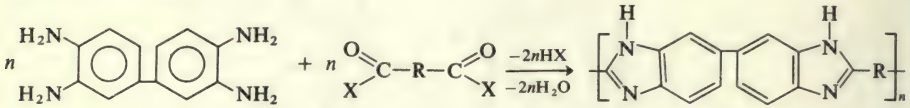
The reaction temperatures and experimental conditions used by Dawans and Marvel (*13*) to form the ladder polymers are shown in Table 19-1.

TABLE 19-1
Information for Preparation of Polybenzimidazolones Ladder Polymers[a]

Starting materials	Experimental conditions	Reaction temp., °C	Repeating unit
Pyromellitic anhydride + 1,2,4,5-tetra-aminobenzene + 1,2,4,5-tetraamino-benzene tetrahydrochloride	Melt Polyphosphoric acid	220–300 220	
Pyromellitic anhydride + 1,4,5,8-tetra-aminonaphthalene	Solution in diglyme	230–300	

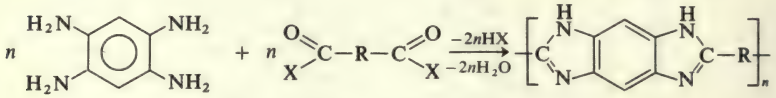
[a] From Reference *13*, courtesy of the *Journal of Polymer Science*.

Actually similar work on high-heat-stable polybenizimidazoles was carried out by Vogel and Marvel earlier (*14*) when they reacted aromatic tetramines with aromatic dibasic acids (or acid derivatives) using melt polycondensation techniques. This work did not lead to ladder structures, however, but rather to semiladder ones:



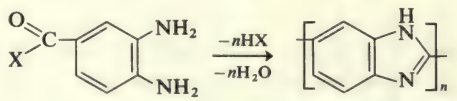
polybenzimidazole

or



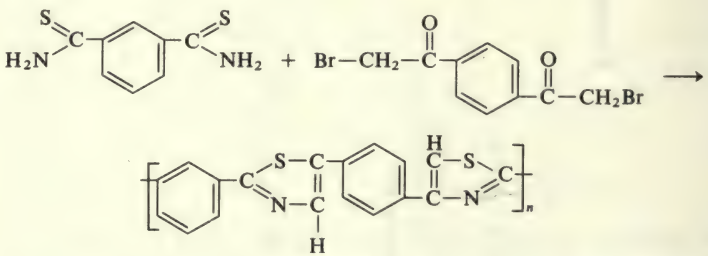
where R = aromatic nucleus, and X = OH, Cl, OCH_3, or OC_6H_5.

A still different method used (*14*) was to have the acid or its derivative and the amine groups on the same molecule,



polybenzimidazole

Such heterocyclic ring formation is, of course, the polymer-forming step. Similar approaches were taken by a number of investigators. Thus as early as 1946 Erlenmeyer and Buchler (*15*) condensed bis-thioamides with bis-halomethyl ketones forming low-molecular-weight products. More recently, Ionu et al. (*16*) and shortly afterward Mulvaney and Marvel (*17*) were able to carry out similar condensations which led to polymers of molecular weights 5000–6000. These thermally stable polymers formed according to the following scheme:

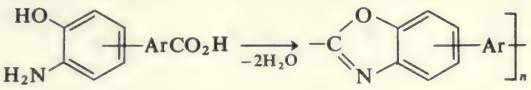


polythiazole

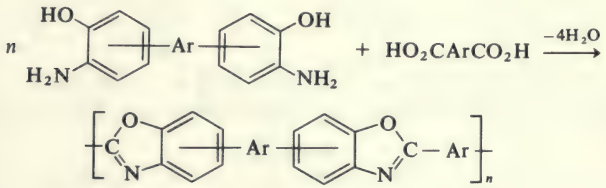
Moyer and co-workers (*18*) carried out condensations of 3,3′-dihydroxybenzidine with phenyl esters of phthalic, isophthalic, terephthalic, and 5-chloroisophthalic acids to form a series of aromatic polybenzoxazoles. Actually, these include two types of materials: those derived from self-contained monomers such as *o*-aminohydroxybenzoic acid and those derived from complimentary

commonomers such as bis-*o*-aminophenols with dicarboxylic acids or their derivatives:

1.



2.



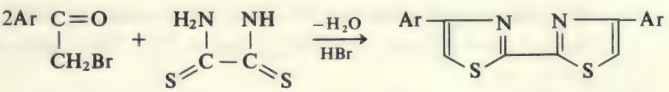
polybenzoxazole

Here too, melt-polymerization techniques were employed which were carried out in inert atmospheres at 250–300°C for 4–28 hours. In the case of 4-amino-3-hydroxybenzoic acid and 3-amino-4-hydroxybenzoic acid, self-condensation was achieved through preparation of an intermediate poly(ester amide) followed by thermal cyclization (at 250–300°C) to the benzoxazole unit.

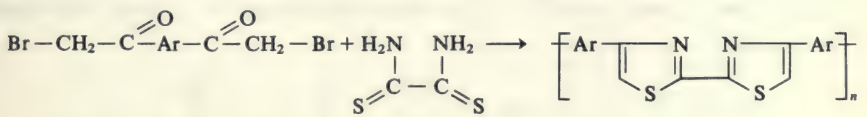
The polymers were all tan-to-brown friable resins which were nonfusible and insoluble in all common solvents except sulfuric acid. These polymers were also quite stable chemically and their thermal stability was similar to polybenzimidazoles.

Other workers have also reported formation of macromolecules with recurring heterocyclic units such as polybenzoxazoles (*19*), polypyrimidonequinazolones (*20*), polyquinoxalines (*21,22*), and so on.

Longone and Un (*23*) reported work on heteroaromatic polybithiazoles. This was done through the condensation of dithiooxamide with halomethyl ketones (*24*),



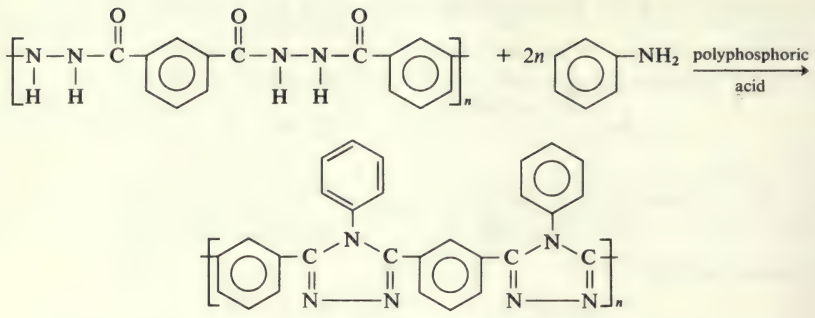
To form macromolecules, difunctional bromomethyl ketones were used:



polythiazole

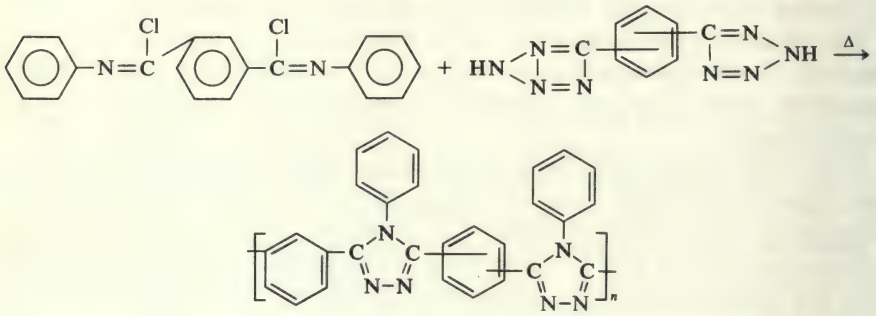
They also found (*24*) that the polymers exhibited outstanding thermal stability, were insoluble, infusible, and, in this case, highly crystalline.

A similar study was done by Liliquist and Holsten somewhat earlier (*25*) when they cyclized polyhydrazides to form polymers containing triazole rings,



polytriazole

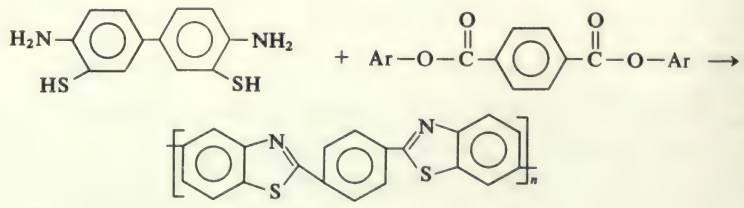
The triazoles used as starting materials for these condensations were originally described by Bates et al. (*26*), who obtained them through fusion of diacid hydrazides in the presence of excess hydrazine. Somewhat similar, low-molecular-weight triazoles were reported by Abshire and Marvel (*27*), who reacted phenylene bis-tetrazoles with N,N′-diphenylisophthalimidoyl chloride,



polytriazole

The polymers obtained by Lilyquist and Holsten (*25*), however, were of high-enough molecular weight to be fiber and film formers. The films also exhibited good thermal stability.

Others followed similar paths. Thus Hergenrother et al. (*28,29*) reported the formation of polybenzthiazoles by the condensation of diphenyl esters of aromatic dibasic acids with bis-orthoaminothiophenols to obtain high-heat-stable polymers,

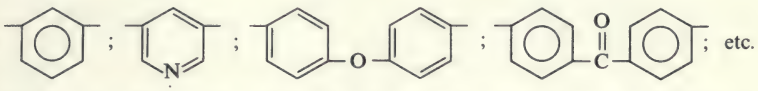


polybenzthiazole

This reaction is quite general and the aromatic diester was only one of the many diacid derivatives studied. It is possible to generalize by describing them as X—Ar—X, where

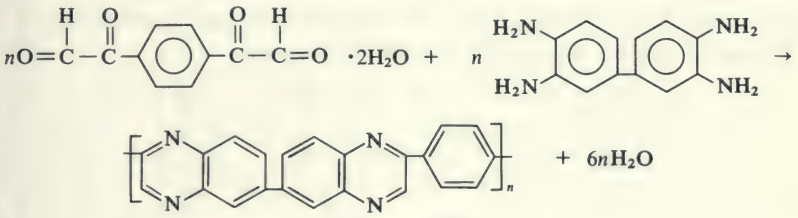
$$X = CO_2H; CO_2R; CONH_2; CN; COCl$$

and

Ar=  etc.

The polymers were found to have excellent oxidative stability at 593°C in air as was determined by low TGA weight loss and absence of changes in infrared spectra.

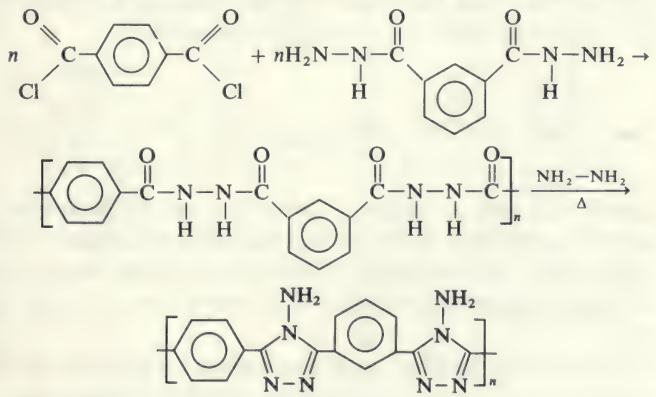
Stille and Williamson (*30*) reacted stochiometric amounts of 3,3′-diaminobenzidine with 1,4-diglyoxalyl benzene using a melt-condensation technique,



polyquinoxalines

A prepolymer was actually formed first in solution. It was then heated in a solventless system to 250°C. Further molecular-weight increases were possible by heating to 375°C under reduced pressure. These polymers were also found to be thermally stable in air at 500°C and exhibited a weight loss of 20% in nitrogen at 800°C.

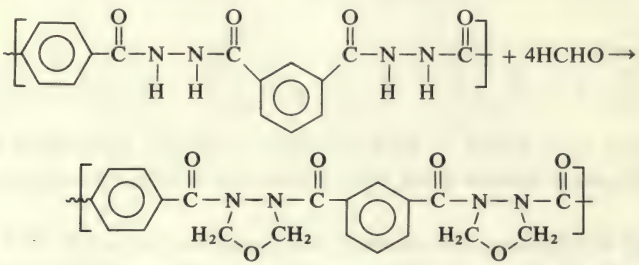
Aromatic polyaminotriazoles were prepared by Frazer et al. (*31,32*), who formed polyhydrazides by first reacting a diacid chloride with isophthalic dihydrazide and then the product with hydrazine under pressure,



polyaminotriazole

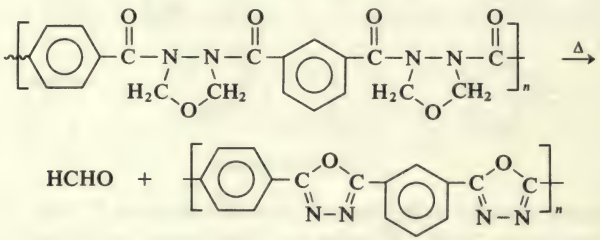
Here, too, the first step was carried out in solution at relatively low temperatures with dimethyl formamide as the solvent.

The same prepolymer can also be reacted with formaldehyde in dimethyl sulfoxide to form corresponding poly(1,3,4-oxadiazolidine),



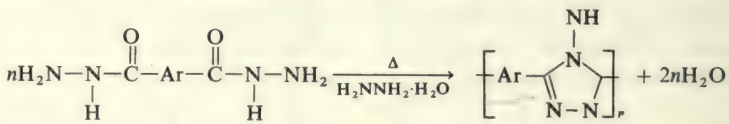
polyoxadiazolidine

Heating this product causes loss of formaldehyde and rearrangement of the heterocyclic ring to the corresponding oxadiazole,



This method actually led to thirteen different aliphatic and aromatic structures (*32*) which had good thermal stability and resistance to oxidative attack at temperatures below 450–500°C. Some general data is shown in Table 19-2 for illustration.

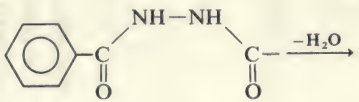
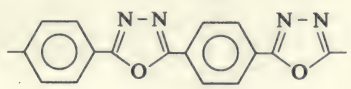
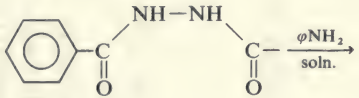
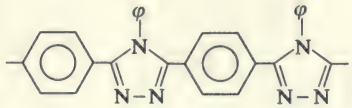
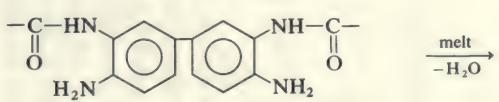
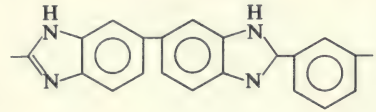
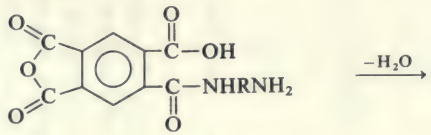
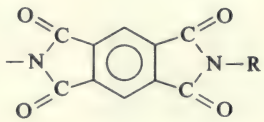
An alternative route to polyaminotriazoles was developed by Stille and Arnold (*33*), who reacted aromatic hydrazides with small amounts of hydrazine hydrate for 6 hours at 300°C and 100 psig pressure followed by additional heating for 12 hours at 300°C and atmospheric pressure,



This approach as well as that of Frazer (*31*) and Wallenberger are adaptations of methods employed to form aliphatic polyaminotriazoles (*34–36*). Both adapted approaches yield aromatic polyaminotriazoles which are soluble in formic acid and dimethylformamide, but which are not high in molecular weight (*33*).

A large number of polymers were synthesized to date in which the chain-stiffening principle was applied to raise the melting temperatures, often up to

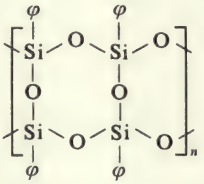
TABLE 19-2
Heterocyclic Analogs of Polyphenylene

Prep. route	Polymer structure	T_g, °C	Approx. M.P., °C	Ref.
		—	>450	31
		—	>500	25
		—	>500	14
		>500	>900	[a]

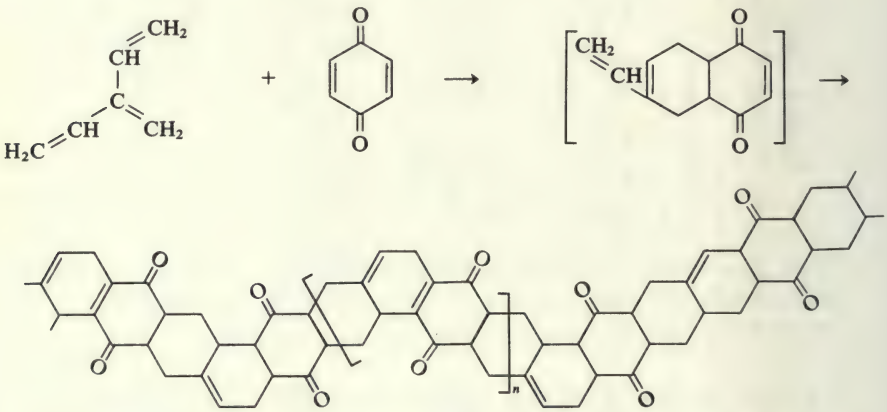
[a] L. E. Amborski, *Polymer Preprints*, **4**(1), 175 (1963).

400°C. Significantly, however, relatively rapid creep often developed at substantially lower temperatures. There is also a certain tendency for environmental stress-cracking.

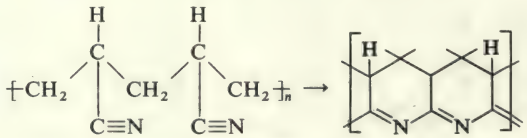
Until now, with a few exceptions (*13*), mostly semiladder polymers were discussed. What about the true ladder polymers? Brown has synthesized (*37*) silicon-containing silsequioxane molecules which may be listed with inorganic polymers,



A true organic ladder polymer was also formed by Bailey and co-workers (*38*) by means of the Diels-Alder reaction,



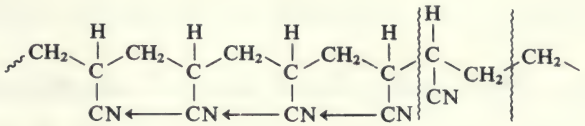
Hurtz (*39*) showed in 1950 that pyrolysis of polyacrylonitrile leads to ladder polymers,



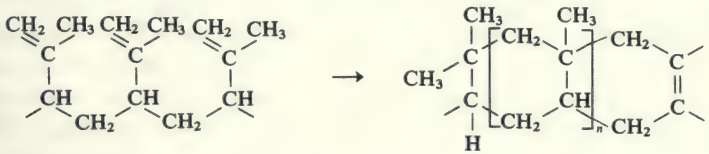
This pyrolytic change occurs at 200–320°C with the evolution of HCN and ammonia and olefins. Bruilant and Parsons (*40*) and later Topchiev and co-workers (*41*) repeated this work and carried the pyrolysis to a black, conjugated structure which exhibited semiconductor properties. The conversion of polyacrylonitrile to a ladder structure results in a 30% loss of weight.

However, lack of perfect head-to-tail structure in polyacrylonitrile formed by free-radical mechanism prevents formation of a perfect ladder structure,

with the result that isolated nitriles are present which are the weak points in the molecule,

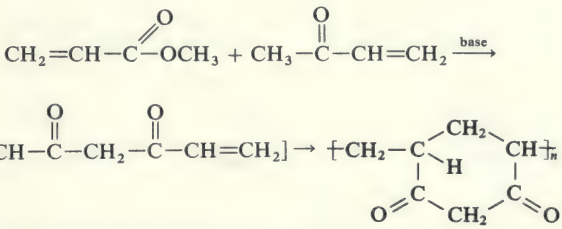


In a very similar manner, all 1,2-polybutadiene should lend itself to cyclization and ladder formation. This was actually accomplished by Angelo (*42*) and also by Gaylord and co-workers (*43*) on 1,2-polyisoprene,

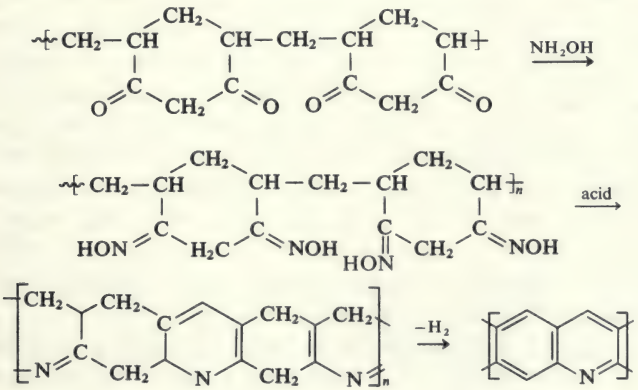


The investigation of the product demonstrated that approximately 18.4% of the groups failed to cyclize, thereby failing to yield a complete ladder structure.

Otsu et al. tried a different approach (*44*), based on a polycyclic ketone as a starting material. The synthesis of such a polymer was reported by Jones (*45*) earlier. It is the result of cyclic polymerization of the condensation product from methyl acrylate and methyl vinyl ketone,



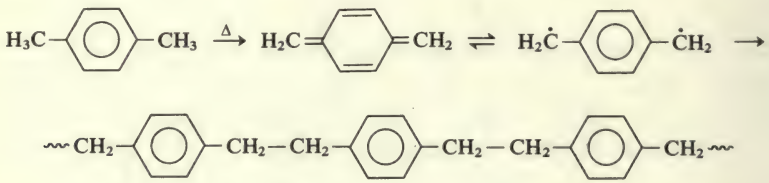
This polymeric ketone was reacted by Otsu et al. with hydroxylamine (*44*),



Unfortunately, however, here, too, a perfect ladder polymer did not form. This Otsu ascribed to the possibility that the Jones polymer probably contained units of methyl vinyl ketone which disrupted the regular structure.

19-2. Polymers with Both Rigid and Flexible Links in the Backbones

As stated earlier, most polymers formed from rigid aromatic cyclic structures are subject to stress-cracking and general brittleness. It appears wise, therefore, not to rely upon any property alone, such as chain stiffness or hydrogen bonding or stereospecificity, to attain desired physical characteristics, but to try and superimpose them in such a fashion that no single feature is magnified at the exclusion of another. It is often desirable, therefore, to strike a compromise for developing optimum properties in the macromolecules. With this in mind, the attention of many investigators turned to macromolecules possessing both rigid cyclic structures and flexible bonds between them. From this viewpoint, poly(*p*-xylylene) should serve as a good example, as it combines rigid benzene rings with elastic ethylene bridges. Such a polymer was actually synthesized early by Szwarc (*46*) and later studied in greater detail by Kaufman et al. (*47*), who also formed polymers of 1,2,4,5-tetramethylbenzene; 1,2,4-trimethylbenzene; 1,4-dimethylnaphthalene; 2,5-dimethylpyrazine; 5,8-dimethylquinoline; and others. The pyrolysis of *p*-xylene leads to this polymer via a diradical intermediate,



The polymer is insoluble and melts at 520°C with decomposition.

The reaction consists (*46*) of a fast flow pyrolysis of *p*-xylene at low pressures with the subsequent condensation of the pyrolyzate into a well-stirred solvent, such as hexane or toluene at −78°C. The resulting solution was shown by Errede to contain *p*-xylene, *p*-xylylene, toluene, *p*-ethyltoluene, styrene, 1,2-di-*p*-tolylethane, diphenylmethanes, diphenylethane, and anthracene (*48–50*).

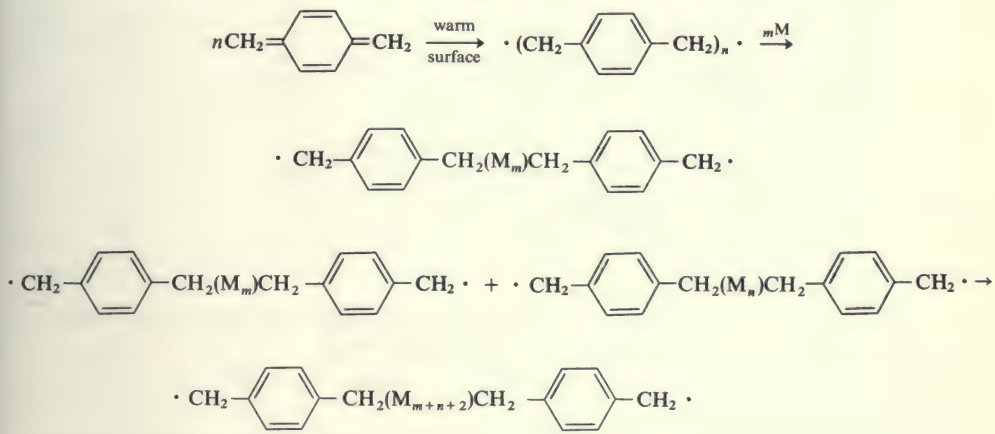
p-Xylelene was found by Errede and co-workers (*50*) to be so reactive that polymerization occurred even at −78°C, whenever the solution was disturbed by momentary contact with a warm surface. This was presumably due to formation of diradicals (*n*-mers) that continued to grow by successive addition of monomer units and/or by coupling. Propagation appears to have continued at that temperature until all monomer was consumed with the formation of a linear polymer of molecular weight greater than 2×10^5.

When the degree of polymerization exceeded 20, polymer molecules precipitated out. The final polymer was obtained in a highly swollen state. Once the

polymer was dried, however, it could not be swollen again or dissolved, except at 300°C in chlorinated polyaromatics.

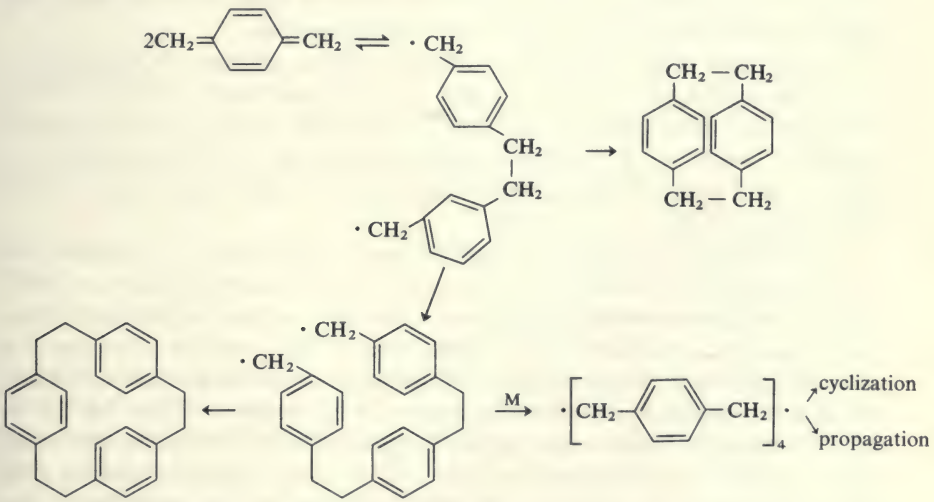
Errede and co-workers (*50*) postulate that two mechanisms of polymerization actually take place, depending upon the conditions being either isothermal or nonisothermal.

Mechanism A: Isothermal conditions at low temperature:



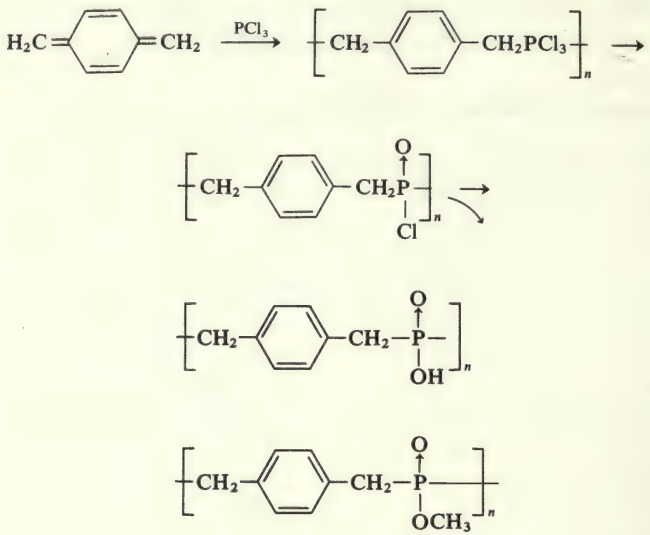
where M is a monomer.

Mechanism B: Nonisothermal conditions (this accounts for the presence of large ring structures in the product):



In addition, Errede and Pearson (*51*) demonstrated that *p*-xylylene can be copolymerized with phosphorus trichloride to form high-molecular-weight poly(*p*-xylylene phosphinic trichloride). The phosphinic trichloride moiety of

the polymer is capable of further reactivity,

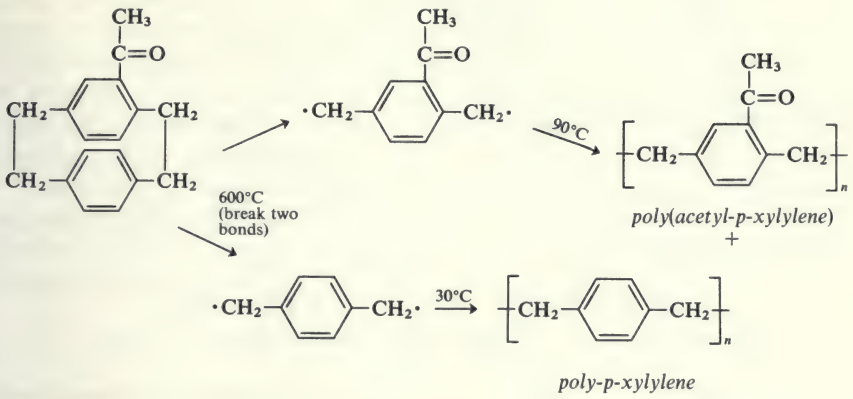


A different approach to the synthesis of polyxylylenes was originally taken by Jacobson back in 1932. He utilized the Wurtz reaction (*52*) on xylylene dibromide to form infusible and insoluble products. Later the dichloride analog was also reacted with sodium metal by Brown and Farthing (*53*). Dioxane was the solvent used. The product appeared to contain some material which was similar to polyxylylene formed via the pyrolytic process.

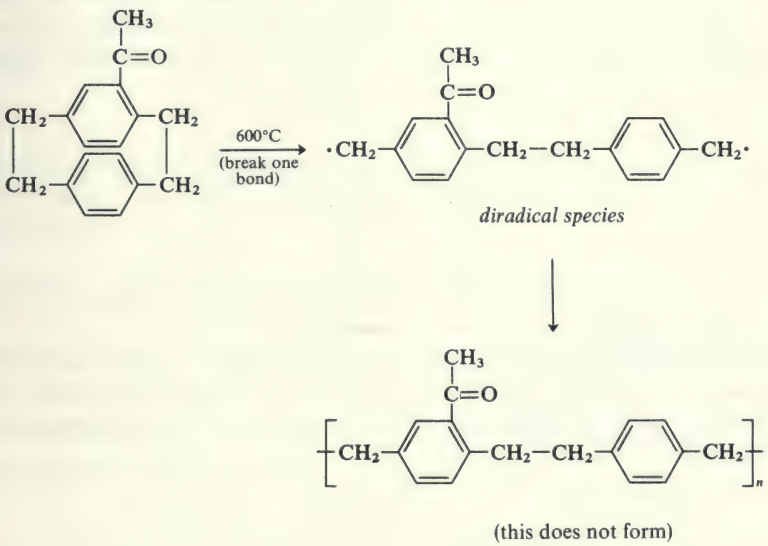
This approach was expanded by Vansheidt and co-workers (*54,55*), who also formed polyxylylene polymers by this reaction, also using dioxane solvent. Both *para* and *meta* xylylenes were used in this study as well as other aromatic homologs, such as 1,5-dichloromethylnaphthalene, 4,4′-bis(chloromethyl)-biphenyl, and so on. Polymers that ranged in molecular weights from 1800 to 4000 were obtained.

Quite recently, the pyrolytic process was investigated by Gorham (*56*). The reactions were carried out in a vapor phase on di-*p*-xylylenes at 600°C, yielding the corresponding *p*-xylylene monomers, which polymerized spontaneously upon condensation on cooler surfaces. The reaction from dimer to polymer appears to be quantitative. By using unsymmetrical dimers, Gorham was able to obtain two different polymers simultaneously. This led him to conclude that the intermediate pyrolytic products are *p*-xylylene monomers and not a mixture of various diradicals. This he feels could be occurring if the reaction proceeds in two ways. If carbon-carbon bonds are broken, di-*p*-xylylene splits into two molecules of di-*p*-xylylene. But if only one bond is broken, then only one molecule of a linear diradical species actually forms. The overall scheme can be shown as follows:

Breaking of two bonds;



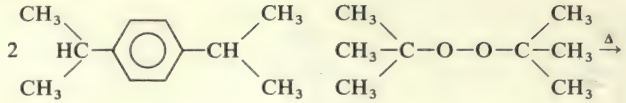
Breaking of one bond (does not occur):

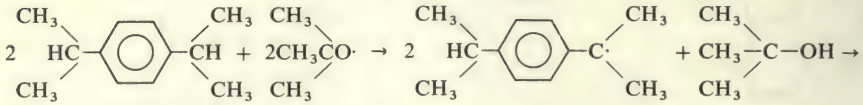


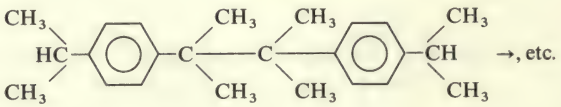
Gorham concluded that polymerization of *p*-xylylenes to poly(*p*-xylylenes) takes place by first condensing two *p*-xylylene molecules on a surface and forming a linear diradical. As *p*-xylylene units attach to each end of the diradical, a linear polymer forms.

In an attempt to form similar polymers, Korshak and co-workers (*57*) formed polymers with alternating rings and alkylidine groups in the backbone by means of a polyrecombination reaction. This was achieved through chain transferring of radicals on diisopropyl benzene by heating it in the presence of

t-butyl peroxide at 170–200°C,

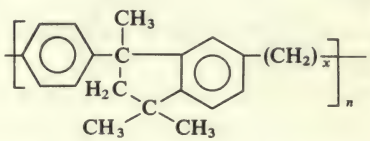






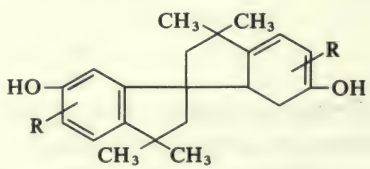
Much of the resulting polymer is insoluble, has a crystalline structure, and melts at about 300°C.

Mitin and Glukhov (*58*) obtained saturated linear polymers which contained phenyl and indane rings by carrying out a cationic-isomerization type of polymerization (see Chapter 5) on diisopropenyldiphenylmethane and on diisopropenyldiphenylethane in toluene solution with $SnCl_4$ and HCl. Polymers with the following repeating units were obtained:



where $x = 1, 2$. For $x = 1$, the polymer shows a softening point of 170°C, and for $x = 2$ the polymer shows a softening point of 130°C.

Following the formation of the polyindanes, Steuben (*59*) prepared polymers possessing 3,3,3′,3′-tetramethyl-1,1′-spirobiindane residues. The starting material here was a class of bisphenols, the 6,6′-dihydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobiindanes,

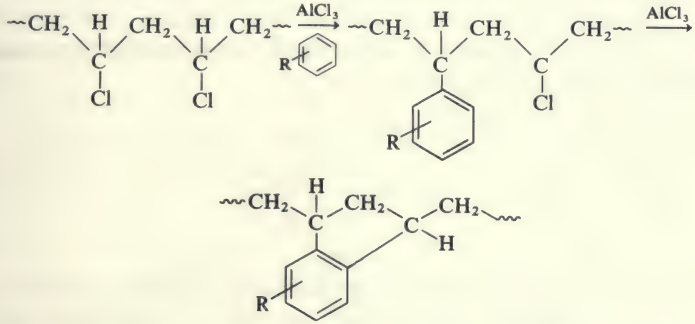


which were converted to the corresponding polyesters, polyurethanes, and polyhydroxyethers. The polycarbonates were found to display good oxidative resistance at 200°C but lacked toughness in spite of $T_g = -100$°C.

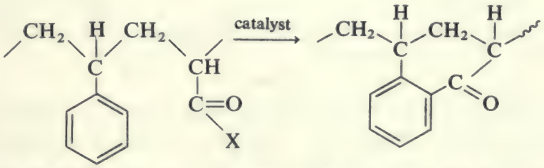
One might include into a discussion of ladder and semiladder polymers a description of a general number of polymers formed with cyclic structures in

the backbone, particularly the products of cyclopolymerization of unconjugated diolefins. The products of such polymerizations, however, contain nonaromatic rings which contribute only a little to the stability of the polymer. This does not mean, however, that considerable effort did not go into formation of polymers with ring structures in the backbones. As a matter of fact, intramolecular cyclization often permits preparation of certain polymers which are unattainable by other means.

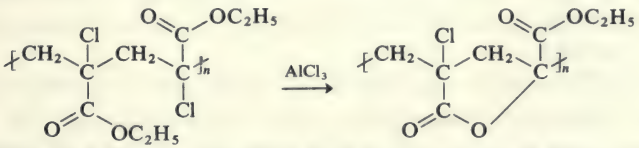
Smets and co-workers (*60–65*), for instance, described the formation of a large number of polymers by such means. One such method is to use a Friedel-Crafts type of reaction (*61*) on poly(vinyl chloride) with benzene leading to chains with indane groups,



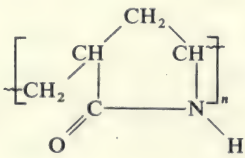
They also carried out (*62*) intramolecular acylation of copolymers of styrene with derivatives of acrylic acid to yield polymers with recurring methylenetetralone groups,



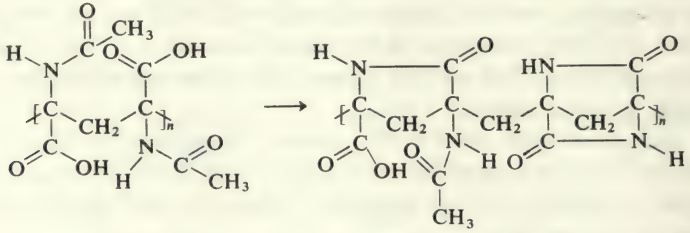
where *X* is Cl or OCH_3. The same method was used to form internal lactone rings in the chain from poly(ethyl-α-chloroacrylate),



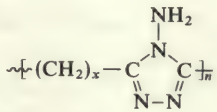
In addition, the Curtius reaction was used to obtain lactam rings in the backbone,



A more interesting double lactam was obtained by means of acid hydrolysis of derivatives of poly(α-N-acetyl) animoacrylic acid, causing internal cyclization,

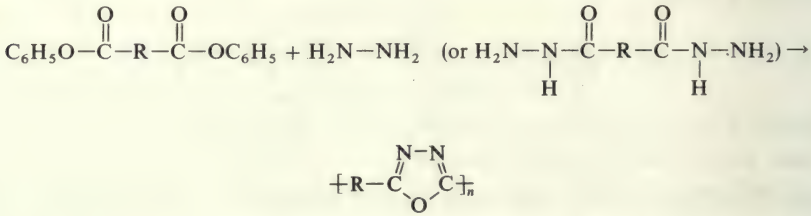


It is also possible to prepare heterocyclic rings alternating with aliphatic groups in the backbone. Thus Erlenmyer and Buchler (*15*) formed polytriazoles with methylene links. Korshak and co-workers (*66*) formed polyaminotriazoles of the general formula



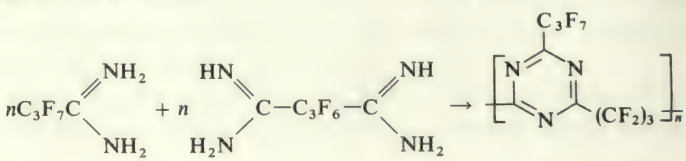
where $x = 2, 3, 4, 7, 8, 20$. The products had relatively high thermal stability.

Unishi and Hasegawa (*67*) formed aliphalic poly(1,3,4-oxadiazoles) through the reaction of equimolar amounts of diphenyl ester of dicarboxylic acid and anhydrous hydrazine or dihydrozide,



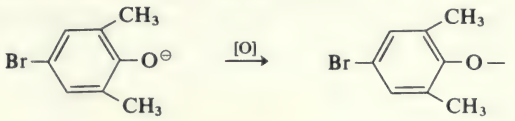
where R is $(CH_2)_8$; $(CH_2)_9$; $(CH_2)_{10}$. The resulting high-molecular-weight polymers are soluble in several solvents, but show very low melting temperature and high crystallinity.

Perfluorinated polymers with heterocyclic rings were formed by Brown (*68*) by condensing perfluorobutyroamidine with perfluoroglutaro- (or adipo-)diamidine. Ammonia is evolved in the condensation, yielding an elastomer with triazine rings in the chains,

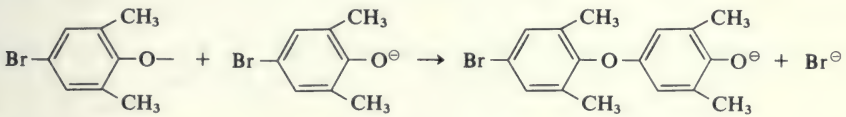


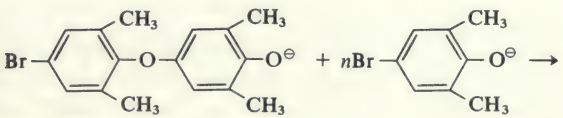
These polymers show good thermal stability with no weight loss in 72 hours at 350°C.

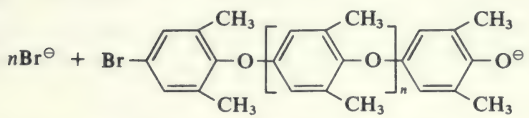
The subject of semiladder polymers should also include aromatic polymers linked by functional groups. Such, for example, are polyphenyl ethers. Staffin and Price (*69*) found that agitation of aqueous solutions of the sodium salt of 2,6-dimethyl-*p*-bromophenol in the presence of oxidizing agents such as iodine, benzoyl peroxide, or lead tetraacetate will cause oxidative coupling,



The polymer then forms through successive liberation of bromide ions,

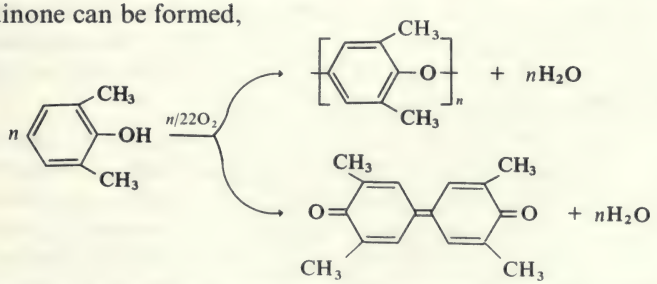






This relatively stable polymer melts at 200°C and has the DP of about 20.

The method appears to have been improved upon by Hay et al. (*70–72*), who found that 2,6-dimethyl phenol undergoes oxidative coupling in the presence of an amine complex of a cuprous salt. A high-molecular-weight polymer or a diphenoquinone can be formed,

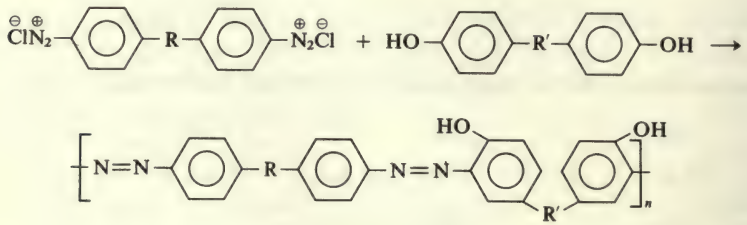


The polymer is soluble in chloroform, *s*-tetrachloroethane, and aromatic solvents, from which films can be cast. This polymer has a softening temperature of 190°C.

It is also possible to form polymers by this method from 2-methyl-6-ethyl phenol; 2-methyl-6-isopropyl phenol; 2-methyl-6-*t*-butyl phenol; 2-methyl-6-phenyl phenol; 2-methyl-6-chlorophenol; 2-methyl-6-methoxyphenol; and 2,6-diethyl phenol.

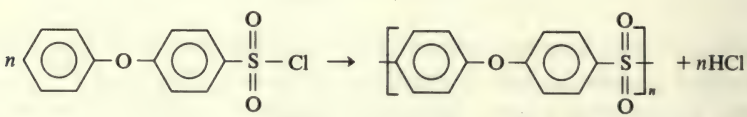
In addition, various aromatic polyesters from aromatic dicarboxylic acids and diphenols were prepared by various investigators and found to be heat-stable (*73,74*). Aromatic polyanhydrides are also known (*75,76*).

Ravve and Fitko (*77*) reported formation of polymers linked by azo groups via diazonium coupling of the diazo salts of aromatic diamines to diphenols,



where R = CH_2; C_2H_4; SO_2; or none, and R′ = CH_2; $(CH_3)_2C$; or none.

Some of the products were dark materials which were high melting and relatively heat stable. The molecular weights ranged from 2000 to 20,000. Cudby and co-workers (*78*) investigated the synthesis of poly(arylene sulfones) by ferric-chloride-catalyzed polycondensations of disulfonyl chlorides with reactive dinuclear aromatic compounds. This was extended to self-condensation of monosulfonyl chlorides to form polymers of high molecular weight,



The investigators found that when catalytic quantities of $FeCl_3$ are used, the condensation proceeds smoothly, more like a Friedel–Crafts alkylation than a conventional Friedel–Crafts reaction. The polymers obtained are essentially linear, as determined by infrared and NMR studies.

It is interesting that Friedel–Crafts synthesis can also be applied to the preparation of polybenzyls and polyphenethyls, as found by Moor (*79*), who reported formation of homopolymers from 2,5-dimethylbenzyl chloride, durylmethyl chloride, 2,5-dimethyl phenyl chloride, and durethyl chloride. The polymers were soluble and fusible. He proposed a linear structure in contrast to infusible and insoluble network polymers obtained by the condensation of benzyl chloride or phenethyl chloride by this method. The polymers were brittle but exhibited good thermal stability.

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Part V

NATURALLY OCCURRING POLYMERS

Polysaccharides

20

Naturally occurring organic polymers can be divided into six main categories:

1. Polysaccharides, a category that includes gums, chitin, pectin, alginic acid, starch, cellulose, and many others.
2. Polypeptides, or naturally occurring polyamides. This large group of macromolecules is found both in the vegetable and animal kingdoms and is the major constituent of such diverse materials as silk, wool, horns, hoofs, feathers, and so on.
3. Polynecleotides, or nucleic acids, found in animal and plant cells and in viruses.
4. Polyisoprenes, the constituent of hevea or natural rubber, balata, and gutta-percha (Chapter 9).
5. Lignins, or polymeric materials of coniferyl alcohol, and related substances found in wood tissues.
6. Miscellaneous polymeric materials found in nature, such as some of the natural resins or, for instance, polyesters found in membranes of certain seeds and lichens.

Each category consists of many materials. Some of these have not yet been investigated. Some may be barely recognized at all. But others are well known. They have been studied and utilized directly or in modified form for many years. Reports in the literature usually describe two types of investigations carried out on such naturally occurring polymers. The first involves efforts to determine the function these materials have in nature. Such efforts either start with or include work on elucidation of structure. The second consists of attempts to utilize these polymers for one purpose or another and often leads to preparation of derivatives to develop or enhance certain desirable properties.

The fundamental chemistry of carbohydrates was established by Fischer (*1*) when he demonstrated the configurational relationships within the monosaccharides.

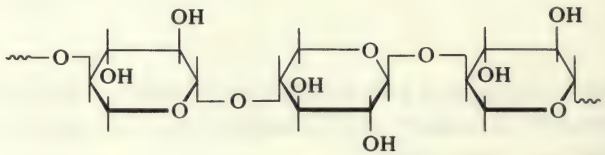
The monomeric species in all the polysaccharides are, of course, the monosaccharides. The simplest combination of these is the formation of dimers or disaccharides. The polymeric materials can be separated into the polymers of pentoses or pentosans and into polymers of hexoses or hexosans.

Hemicelluloses are not defined exactly, either analytically or experimentally. When hydrolyzed, the products are a mixture of glucose, glucuronic acid, xylose, arabinose, galactose, galacturonic acid, mannose, and rhamnose.

20-1. Pentosans and Minor Hexosans

Following are some of the pentosans and hexosans.

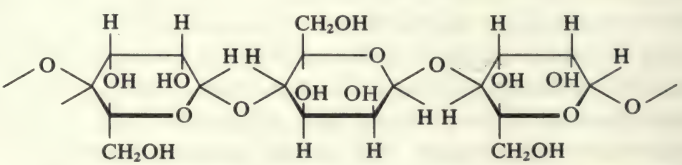
1. *Xylan* is found in liquified cell membranes. Structure elucidated by Haworth et al. (*2*) demonstrated that the material is a 1,4-polyxylose,



2. *Araban* is composed of arabinose. This natural polymer occurs in small quantities.

3. *Galactans* are found in small quantities in some coniferous and deciduous woods. Thus, according to Svedberg (*3*), larch wood contains about 8% of this polysaccharide. It is composed of two nearly monodisperse components with molecular weights of 16,000 and 100,000 in the proportion 1:4. The former is an arabogalactan, the latter a β-galactan containing in equal proportions two types of galactan residues: (1) those linked with their neighbors through atoms 1, 3, and 6 and (2) those linked through 1, 6, and 1.

Mannans. This hexosan yields mannose on hydrolysis. These polysaccharides are known to possess mechanical properties similar to cellulose. They are contained in the thickened cell wall of hard seeds and form the chief constituent of the American ivory nut. Meyer and Mark (*4*) suggested that the structure of mannans is probably



This structure was later confirmed by the work of Klages (*5,6*) and Mavenbrecher (*7*).

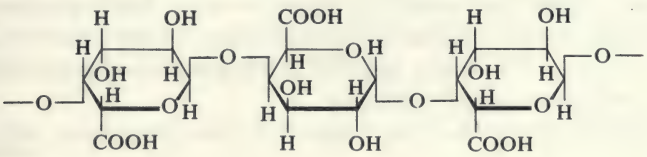
Pectins. While glucose forms the structural unit of the skeletal and reserve substances of plants, galacturonic acid and arabinose form the structural units

of a group of carbohydrates characterized by their great swelling power in water. Their presence might be tied up in various biological functions.

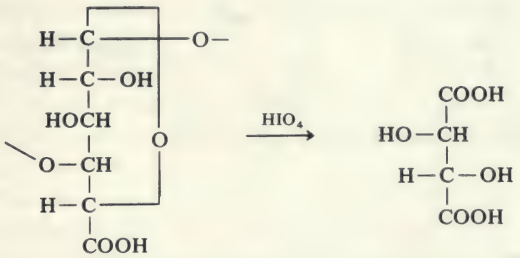
Ehrlich and Sommerfield (*7*) and Ehrlich and Schubert (*8–10*) have shown that the complete hydrolysis of pectin yields D-galactose, D-galacturonic acid, and L-arabinose.

Pectin, which is insoluble in cold water, is slowly dissolved by heating with water under pressure. Extraction with 70% alcohol removes a soluble araban and the remaining calcium-magnesium salt gives, on complete hydrolysis, galactose, arabinose, galacturonic acid, and methyl alcohol. A mild hydrolysis yields a poly(galacturonic acid).

Smolenskii (*11*) proposed a linear, high polymeric structure for pectins and a highly branched structure for poly(galacturonic acid). But Meyer and Mark (*4*) felt instead that poly(galacturonic acid) probably is also linear,



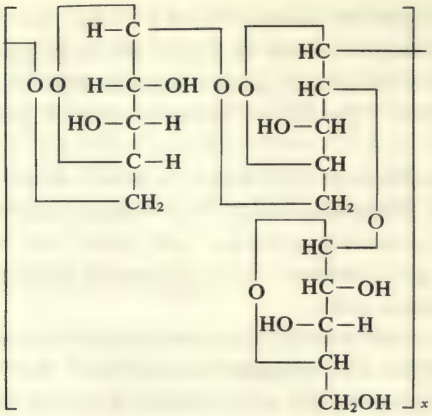
Such a structure is fairly well accepted today as a result of numerous studies. Furthermore, investigation by Link and co-workers (*12–14*) has led them to advocate a 1,4-glucosidal linkage for the units. Levene and Kreider (*15*) confirmed this by direct chemical evidence. They carried out periodic acid oxidation and obtained tartaric acid as a result,



Levene et al. (*16*) prefer the furanose to the pyranose form, as being more likely.

The relative amounts of the various constituents in pectine vary considerably. Thus, for example, citrus pectin is very rich in galacturonic acid but poor in galactose and arabinose. At the same time, flux pectin was reported (*17*) to contain no galactose and only 0.5–3% arabinose.

The galactans are pictured as consisting of chains of galactose residues also linked in the 1,4 positions.

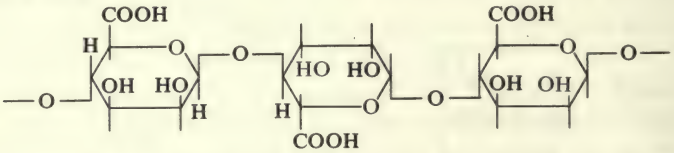


Plant gums. Gums and mucilages occur in many different plants. These are high-molecular-weight polysaccharides in which hexose, pentose, and uronic acid units are linked with one another. More work is needed to determine the structure and nature of their linkages.

They include gum arabic, gum tragacanth, plant mucilages, and alginic acid.

20-2. Carbohydrates from Algae

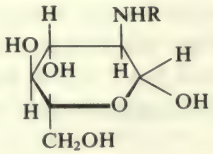
Polymeric acids can be isolated from algae. Nelson and Cretcher (*18–20*) described them as being polymanuronic acids. Klingstad and Lunde (*21*) suggested that the molecular weight might be similar to that of cellulose, and the structure may be



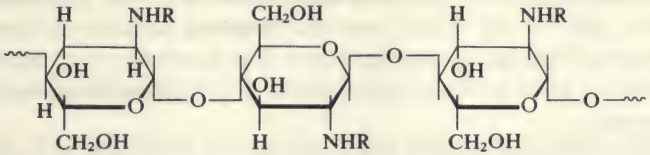
This was confirmed by Lucas and Steward (*22*).

20-3. Chitin

The organic skeletal substance of anthropods, annelids, mollusks, and fungi is chitin, a nitrogen-containing carbohydrate. The constitution of chitin was studied by Karrer and Mayer (*23*) and by Haworth et al. (*24*). They concluded that the polymeric material was made up of glucosamine units,



The formula proposed by Meyer and Mark (*25*) was confirmed by Bergmann and co-workers (*26*), and by Zeichmeister and co-workers (*27,28*), to be



Until now mainly the naturally occurring polymers of aldoses were mentioned. Nature is also very abundant in polymers and copolymers of ketoses. Polyketohexoses are very varied in structure and degree of polymerization. Thus there are branched and unbranched as well as high- and low-molecular-weight polymers throughout the vegetable kingdom. The optical rotation may be positive (phlein) or negative (inulin). These materials can usually be found dissolved in cell sap. Inulin, however, can be found in tubers. Alcohol-precipitated inulin is amorphous. It crystallizes slowly from water solution. Molecular weight of Dahlia inulin is from 3000 to 5000.

20-4. Starches

Starch, by being the chief reserve carbohydrate of plants, is one of the most widely distributed substances in the vegetable kingdom. In its composition and structure it is a high polymeric carbohydrate. The repeating unit is glucose and the monomeric units are presumed to be joined by glucoside linkages, because substantially, 100% theoretical yields of glycose may be obtained by hydrolyzing starch at low concentration in diluted aqueous acidic solution. Starch shows initially only a very feeble reducing power but, as hydrolysis proceeds, the ability to reduce, as, for example, an alkaline solution of copper sulfate, progressively increases.

Diastatic enzymes hydrolyze starch and the principle end product in this case is maltose. Under favorable conditions some starches yield as high as 70–80% of this sugar, which consists of two glycopyraniside units joined by a 1,4-α-glucosidic linkage. Considerable chemical evidence has been compiled (*29*), which supports the view that this linkage is the principal polymeric bond.

Considerable evidence now also exists that chemical bonds other than 1,4-α-glucosidic linkages are also present in starch, and the recent main problem in starch chemistry has been the determination of the nature and number of these bonds and the distribution of these anomalous linkages throughout the starch structure.

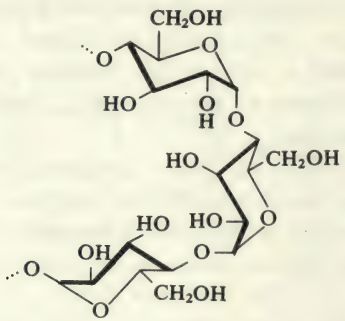
The common starches may be fractionated by physical, or physical-chemical methods into components which differ in both chemical properties and physical behavior. Accordingly, it becomes evident that compared to many other carbohydrates, starches are relatively heterogeneous. The view is now accepted that the majority of starches contain molecules which can be classified according

to one or two different structural patterns. One type is a linear polymer with the polymeric bonds of the glucopyranoside units being substantially all 1,4-α-glucosides. The other type also contains a very large proportion of these linkages, but periodically throughout the structure, linearity is interrupted by some anomalous linkage, a 1,6-glucoside which would serve to connect another chain of glucose units to the primary chain of anhydromaltose units and thus create a branch.

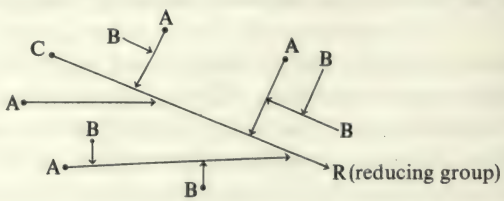
A considerable range of sizes exists among the molecules of each structural type, even in any one variety of starch. Furthermore, among the nonlinear molecules there are variations in the frequency with which linearity is interrupted and in the length of the terminal branches. Nevertheless, to simplify the subject, the custom has prevailed to classify starch polymer fractions on the basis of molecular linearity or nonlinearity. The linear starch is called *amylose*, and the nonlinear, *amylopectin*. This classification can be called superficial and arbitrary, because of the obvious possibility of exceptions.

Molecular-weight determinations on amylose and amylopectin by physical methods such as ultracentrifugation, light scattering, osmotic pressure, and viscosity measurements are difficult, as amylose readily retrogrades from solution. Nevertheless studies indicate chain lengths of 3800 units (*30*). End-group analysis by periodate oxidation indicated chain lengths of 250–1000 units for amylose (*31–34*). Here too, some degradation and overoxidation is possible.

A spiral form is pictured for amylose due to the conformation of α-glucosidic bonds (*29*),



On the other hand, a ramified structure is most likely for amylopectin. Such a structure is supported by results from enzymatic degradation (*35,36*),



In the above picture, A denotes those chains which are linked solely through their reducing group to the rest of the molecule, and B denotes chains which are attached but which are themselves similarly linked to other chains. C denotes chains with a free reducing group R.

Crystalline Forms of Starch

Two main types of crystal structure are found in native starch granules (*37*). These are designated A, representing the cereal starches, and B, representing the tube starches, with the intermediate types between the extremes called C types.

On crystallization of starch from aqueous pastes regardless of source, A, B, or C types of crystallization can readily be obtained, depending on the temperature of preparation. In general, the B type of crystallization is obtained by evaporation of pastes at room temperature or by precipitation of insoluble starches by freezing or retrogradation; the C type at a temperature somewhat above room temperature; and the A type at temperatures about 80–90°C. At higher temperatures, only amorphous preparations are usually obtained. The crystal unit cell parameters of A and B types, according to Bear and French, are given in Table 20-1.

When starch pastes are precipitated with alcohols or some other precipitating agent, a different type of crystallization takes place (*15*). The X-ray diffraction pattern of alcohol precipitated starch shows the "V" pattern (Verkleisterungspektrum, or paste form). It is much simpler than the A or B type of pattern, indicating a more symmetrical arrangement of molecules. The starch thus precipitated also differs notably from granular starch in other respects. Freshly precipitated starch of the V type is readily dispersible, often in cold water; on standing the material gradually loses its solubility in water, and if allowed to stand moist, retrogrades to the B configuration. The very important property of alcohol-precipitated starch of the V configuration is its ability to take up large amounts of iodine vapor.

Starch pastes precipitated with an excess of ethanol or propanol are coarse and formless, and the X-ray diffraction of V pattern consists of only three or four, more or less sharp lines. When higher alcohols, however, such as butanol or amyl alcohol are used, a fine crystalline precipitate forms slowly and then the X-ray pattern is relatively rich. Upon drying, the simple V pattern is re-established.

TABLE 20-1[a]

Type	a_0(A)	b_0(A)	c_0(A)	Alpha	Beta	Gamma
A	15.4	8.87	6.18	87.0°	86.9°	92.8°
B	16.1	9.11	6.34	90.0°	90.0°	90.0°

[a] From Reference *37*.

Optical Rotation of Starch

Most values for the specific rotation of starch range between $[\alpha]_D = 180$ and 220°. Literature reports many different values and the results are confusing. By comparison, most values reported for hydrolytic dextrins of high molecular weight which are readily soluble lie between $[\alpha]_D = 190$ and 220°.

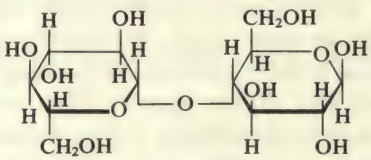
20-5. Cellulose

Cellulose often denotes a fibrous vegetable product, the main component of which is a water- and alkali-insoluble polysaccharide: 1,4-β-polyanhydroglucose, actually a mixture of such homologs.

The pure celluloses can also vary with respect to chain lengths, crystallinity, and arrangement of chains. Thus one must qualify one's statements in speaking about cellulose in general terms.

Cellulose comprises the main constituent of the walls of nearly all plant cells, with the exception of fungi, where it is replaced by chitin.

All celluloses can be decomposed with strong acids to yield glucose. This fact, known for a long time, does not explain the nature and position of linkages. The first step in elucidating this came from the work of Franchimont (*38*) and Skraupt (*39*), who demonstrated that a disaccharide, cellobiose, can be obtained by the acidolysis of cellulose,



Furthermore, the reaction conditions were such that cellobiose could not arise from glucose. The important aspect of cellobiose is the fact that it possesses a β-glucosidic linkage, being a β-glucosidopyranose (*40*). Isolation of cellobiose led to the conclusion that cellulose was composed of β-linked glucose units (*40–42*). This idea was further confirmed by isolation of cellotriose, cellotetraose, and cellohexaose (*43*). Thus the "ideal" molecule is a linear polymer composed of individual anhydroglycose units (also called *glucopyranose units*), linked at the 1 and 4 positions through glycosidic bonds with the beta configuration (*44*). Even though cellulose comprises approximately one-third of all vegetable matter, the mechanism of its formation is still being argued.

A structure of cellulose that will explain many of its properties can be drawn. Such a structure should show the chain configuration of glucose units, and the axial and equatorial positions of hydroxyl groups,

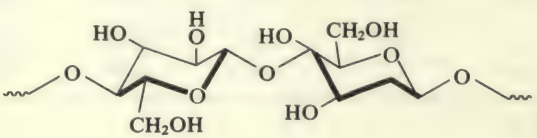


TABLE 20-2
Molecular weight of Celluloses[a]

Cellulose	Mol. wt.	DP
Flax	5,900,000	36,000
Ramie	200,000	12,400
Cotton	175,000	10,800

[a] From Reference *46*.

Three hydroxyl groups per each anhydroglucose unit as well as the configuration of pyran rings permit many hydrogen bonds along the polymer chain. These bonds plus the van der Waal's attractions hold together positions of the chains into different degrees of lateral order which range from a perfect or nearly perfect geometric packing of crystal lattice to random configurations.

Staudinger and Schulz (*45*) concluded that the molecular weight of cotton cellulose is 16,200 (DP = 1000). This was later proved to be in error. Gralen and Svedberg (*46*) found that it is actually much higher by the ultracentriguga-tion methods. The molecular weights of some celluloses are shown in Table 20-2. Now it is generally agreed that native cellulose has a molecular size greater than 3000 anhydroglucose units (*29*).

Cellulose in its native form is highly crystalline and its T_m is far above decomposition temperature. The solubility of this polymer is very low, owing to strong intramolecular forces and crystallinity. It has been suggested that in cellulose there is a gradual transition from the crystalline to the amorphous region and back again. The crystalloids are long and rod-shaped. In ramie, the size of these crystals is 50–100 A in diameter and 500–600 A in length. Per cent crystallinity in some cellulose is shown in Table 20-3.

TABLE 20-3
Degree of Crystallinity of Some Celluloses from X-ray Diffraction Data[a]

	Crystallinity, %
Cotton	69.9–70.0
Ramie	70.0–70.5
Viscose rayons	26;38.0–40.0
Mercerized ramie	47.0–51.0
Valonia ventricosa	68.0–69.0
Bacterial cellulose	70;40

[a] From Reference *47* and other literature sources.

The X-ray diffractions suggest screw-shaped chains, linked together by H bonds that may link the chains together into sheets. Infrared data suggest that all hydroxyl groups of cellulose are hydrogen-bonded (*48*).

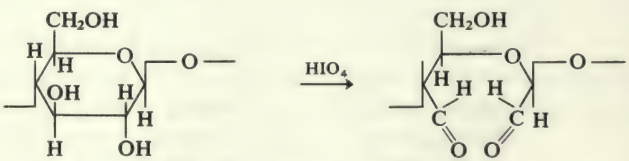
Degradative Processes

The fine structure of cellulose is very important in determining the course of reactions as well as the properties of the products. Specifically, reactions carried out on dilute solutions of cellulose occur at random sites along the chain backbones because the chains are unraveled and the sites accessible. On the other hand, reactions carried out on fibrous cellulose (which are actually more common) occur rapidly in the amorphous regions, where the sites are accessible, but only slowly in the crystalline regions, which possess high lateral order. This is very pronounced with reactions involving hydroxyl groups. The properties of the products depend largely on the extent of reaction and also on the distribution of reaction sites.

The volume of work on chemical reactions of cellulose is very large. Much of it was done to develop new derivatives for various uses. Much of it was also done to determine structure or to elucidate mechanism of degradation. Such degradation, whole or partial, may be achieved with the aid of acids, oxidizing agents, or bases. When acids or oxidizing agents bring about partial degradation, the products are known as *hydrocelluloses* and *oxycelluloses*, respectively. Generally, it is agreed upon (*29*) that formation of hydrocelluloses by the action of acids on cellulose consists solely of the hydrolysis of glycosidic linkages. Sharples (*49*) has proposed that such acidic hydrolysis takes place first through the glycosidic bonds readily available in the amorphous regions of cellulose. When all the amorphous material has been dissolved, then degradation proceeds very slowly by an endwise attack on the crystallites, with single molecules of glucose being severed successively from ends of the chain molecules.

The mode of attack of many oxidizing agents on cellulose is not fully established as yet. However, two oxidizing agents, periodic acid and nitrogen dioxide, were studied extensively, and their mode of action is fairly well established.

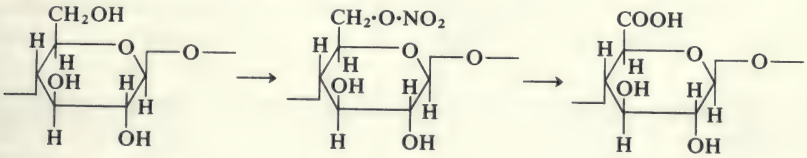
Jackson and Hudson (*50*) demonstrated that periodic acid converts each chain unit to a 2:3 dialdehyde unit (Malaprade reaction),



The effect of pH on this reaction is quite similar to that of periodate oxidation of simple glycols.

When cellulose is oxidized by nitrogen dioxide, the main reaction is the conversion of primary alcohol groups to form uronic acid. McGee and co-workers

(*51*), who studied this reaction, concluded that the oxidation proceeds by way of cellulose-6-mononitrate intermediate, which then converts to uronic acid by a combined process of denitration and oxidation.



Cellulose is attacked slowly by hot alkali with the weight loss being a function of the number of aldehydic groups present. Davidson (*52*) suggested that scission occurs by stepwise processes from the terminal reducing ends. Several theories exist about the mechanism of alkali degradation of cellulose. The picture, however, still is not clear and requires further study.

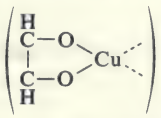
Compounds of Cellulose

Water and ammonia swell cellulose by breaking hydrogen bonding. Aliphatic amines will form addition compounds. Alkali will swell and dissolve cellulose.

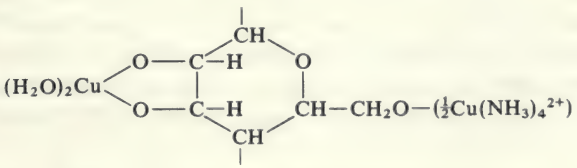
Native cellulose can be dissolved in $CuO—NH_4OH$ solution, from which it can be regenerated by treatment with acids or alkali. The whole reaction is still not fully elucidated. We know that it is not a simple alcoholate formation. We also know that NH_3 is set free from the complex ion.

$$Cu(NH_3)^{2+} + \text{cellulose} \rightarrow NH_3 + \text{complex}$$

and it might be speculated that the complex copper forms ring structures,

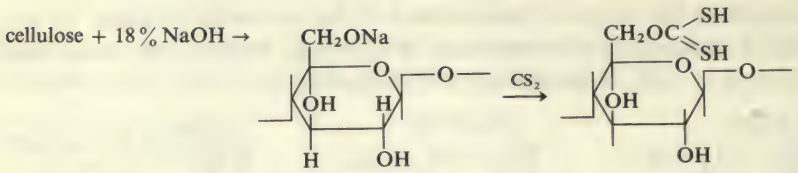


The same might be guessed for the reaction of cellulose with ethylene diamine. So the picture of the complex might perhaps look like this:

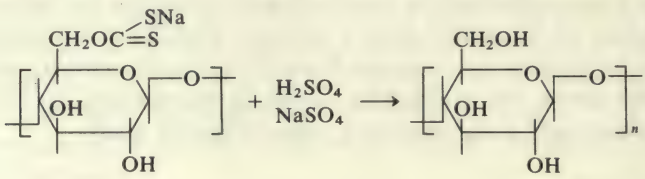


It is interesting that cellulose can be reprecipitated back with weak acids or neutral precipitants (salts) without changes in viscosity.

Another process of cellulose regeneration is through the viscose process, where cellulose is first swelled with sodium hydroxide and then reacted with CS_2,



The regeneration step involves decomposition of the CS_2 adduct under acidic conditions,



Cellulose Esters

Cellulose acetate is one of the more important synthetic esters of cellulose. A quick glance at the structure of the starting material will reveal that it should be possible to form a triacetate. And, actually, cellulose triacetate was synthesized originally many years ago.

Nevertheless, the so-called *secondary acetate*, one possessing on the average 2,4-ester groups per each anhydroglucose unit is often preferred commercially, owing to lower hydrophobic character and greater solubility in such solvents as acetone.

Three commercial processes are generally employed for the preparation of cellulose triacetate. Two of these involve solution of cellulose in the acetylating mixture, whereas the third is carried out under heterogeneous conditions in which the cellulose does not dissolve. The first is the Dreyfus process (*53*), in which relatively large quantities of sulfuric acid are used for acetylation in acetic acid + acetic anhydride + sulfuric acid mixture.

The second process, developed in Germany, employs methylene chloride as the solvent for the formed cellulose ester (*54*). Here much smaller quantities of sulfuric acid can be used, owing to solubility in methylene chloride of the formed ester. Catalysts such as perchloric acid are often employed. The third process consists of acetylating with acetic anhydride, but in a nonsolvent such as benzene.

Throughout the large volume of publications on cellulose one can find a vast variety of esters reported for cellulose. Commercially, however, most have not attained special importance, with the exception of mixed esters such as cellulose acetate–butyrate, which is manufactured by carrying out esterification with a mixture containing acetyl and butyryl radicals. Sulfuric acid is usually the most useful catalyst.

Cellulose Ethers

The etherification of cellulose can be accomplished in several ways. The most usual way is to react alkali cellulose with alkyl halides to form cellulose ethers and salts. One can also resort to carrying out reactions with ethylene oxide and its derivatives. Diazomethane may also be used to form methyl ethers. Very high substitution is hard to achieve, owing to inaccessibility of reactive cites. This can be overcome in methylation. Mixed ethers can be formed easily (*55*).

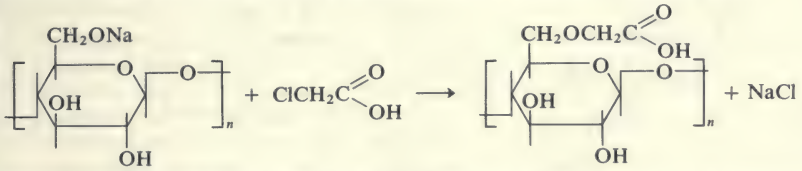
Methyl cellulose is formed industrially by reacting alkali cellulose with methyl chloride. The commercial cold-water-soluble product ranges from 1.5 to 2.0 ether groups per each anhydroglucose unit. Water solutions of this ether tend to jel or precipitate upon heating. Products with 2,5 substitutions are insoluble in water. When the reaction is carried out in a homogeneous condition (in quaternary ammonium bases) leading to random substitution, water solubility is achieved at a substitution of less than 1.

Ethyl cellulose is formed commercially in a similar manner, using ethyl chloride and alkali cellulose (*56*). At a substitution of about 1, the polymer is water-soluble (*57*), but the usual product, which is substituted 2,2–2,8, is soluble in organic solvents only.

Benzyl cellulose is manufactured in Europe (*58*) from benzyl chloride and alkali cellulose. Other aromatic groups may also be used. Thus triphenyl methyl chloride is used in reactions with cellulose. This is a way to distinguish primary hydroxyl groups, with which it will react rapidly in the presence of pyridine at 100–120°C, from secondary hydroxyl groups with which it will react only slowly (*59,60*).

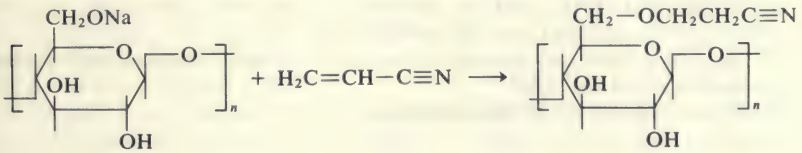
Carboxymethylation is a useful commercial reaction. A typical commercial product of slightly less than 1 substitution is usually a sodium salt. High substitution is possible (*61,62*).

The reaction is carried out on alkali cellulose with chloroacetic acid,



Higher alcohols may also be used as the reaction medium. Other solvents have been employed with the reaction taking place at room temperature (*63*). It was reported that carboxyethyl cellulose was formed in a similar manner (*64*).

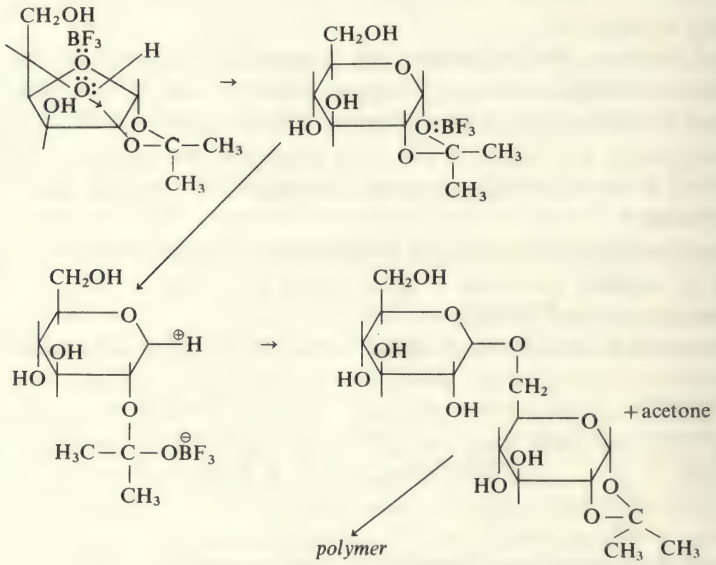
Cyanoethylation of cellulose is a case of a Michael addition of acrylonitrile to alkali cellulose (*65,66*),



The cyanoethyl ether is not as resistant to hydrolytic attack as other ethers, owing to the effect of the nitrile group. Other activated olefins may be used in this reaction as well, such as acrylamide, which reacts readily (*67*).

20-6. Synthetic Polysaccharides

Polysaccharides, as naturally occurring macromoles, are interesting enough to be studied and perhaps modified for use. In addition, glycose and the other monosaccharides are potential monomers for polymer syntheses. Seib and Whistler (*68*) demonstrated that acetone derivatives of D-glucose and some other monosaccharides can be polymerized. The method appears applicable to sugar 1,2-ketals and perhaps acetals, with BF_3 used as the catalyst. The reaction on diacetone glucose can be carried out in benzene at 65°C to yield a polymer of molecular weight of 5230 in 12 hours. The monoacetone glucose condenses much faster. In the melt at 165°C, a molecular weight of 13,000 can be attained. The mechanism is believed to involve a ring expansion,



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Proteins

21

By far the largest group of naturally occurring macromolecules are the proteins. They vary tremendously in properties and infinitely in the functions they perform. One need only consider the fact that silk, horn, keratin, and tendon all consist of proteins. In addition, they can be rubberlike in elastic fibers or contractile in muscles. Proteins also perform catalytic functions as enzymes in most biological processes. A thorough discussion of the chemistry of proteins is beyond the scope of this book.

Our knowledge of protein morphology has expanded considerably over the last 15–20 years. Originally the protein molecule was regarded as being spherical. Meyer and Mark (*1*) were the first to demonstrate that actually the protein in silk threads has the shape of long chains. In addition, they were able to interpret the lattice structure of silk as a primary valence chain in which the length of a peptide unit is 3.5 A.

Later it was found (*2*) that in all fibers composed of proteins, the stretched primary valence chains are arranged parallel to the fiber axis, and that under certain conditions these chains are able to change their shape and fold up. This led to the separation of proteins into two classes: fibrillar and globular.

Proteins are all naturally occurring polycondensation products of not more than approximately 20 different kinds of α-amino acids, which have the general formula of $NH_3^{\oplus}CHRCO_2^{\ominus}$. These exist in aqueous solution as dipolar ions. The amino acids differ in the nature of the R group, which can range all the way from a methyl group, as in alanine, to a phenolic group, as in tyrosine. The function of the carboxylic and animo groups is to act as combining links with the amino and carboxylic groups of other amino acids by forming polyamide linkages.

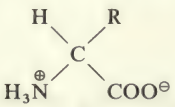
All amino acids found in proteins (with the exception of glycine) possess the same steric configuration of substituents around the optically active α-carbon atom. If the α-carbon is placed at the center of a tetrahedron with the proton

at the top, then one will find the amino group, the carboxyl, and the side group arranged clockwise around the base. This, of course, is the L configuration.

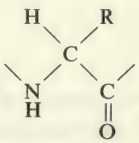
It should be clear that whereas the fundamental repeating structure of the protein molecule is analogous to synthetic polyamides, proteins differ in the fact that there is great variety in monomer units within each polymer structure and in the magnitude and variety of the intermolecular forces which the polar and charged groups on the side chain can exert on each other and on the surrounding molecules. These factors are of primary importance to protein structure (*3*) and result in highly organized corpusecular molecules of a type still unknown in any synthetic polymer.

Following is a simple tabulation of the monomeric units or the L-amino acids commonly found in proteins:

In free amino acid:



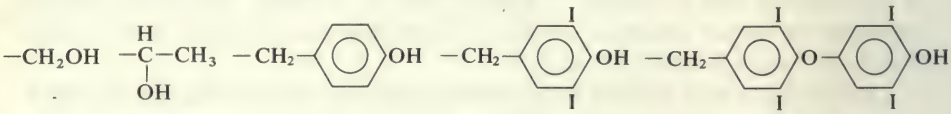
In a peptide chain:



Group 1: Nonpolar Aliphatic R Groups

glycine *alanine* *valine* *leucine* *isoleucine*

Group 2: Hydroxyl-Containing R Groups, Aliphatic Aromatic

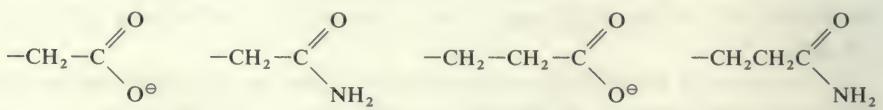


serine *threonine* *tyrocine* *diiodotyrocine* *thyroxine*

Group 3: Other Aromatic R Groups

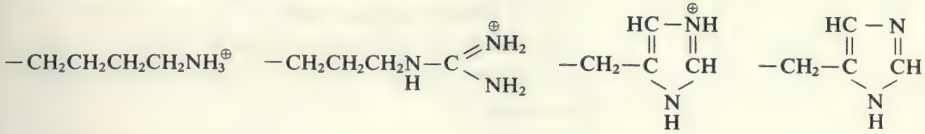
phenylalanine *tryptophan*

Group 4: Aspartic and Glutamic Acids and Their Amides



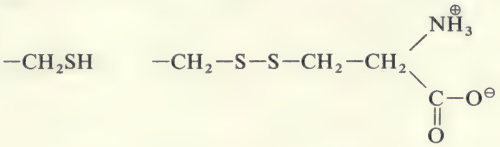
aspartic acid *asparagine* *glutamic acid* *glutamine*

Group 5: Basic Amino R Groups

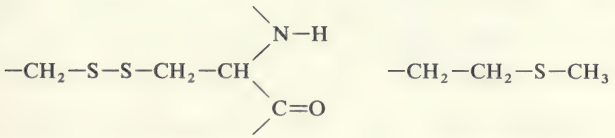


lysine *arginine* *histidine* *histidine (basic form)*

Group 6: Sulfur-Containing R Groups

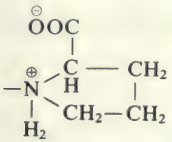


cysteine *cystine (a)*

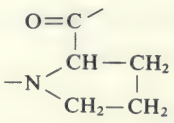


cystine (b) *merthionine*

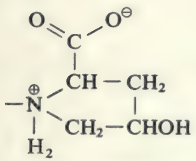
Group 7: Amino Acid R Groups



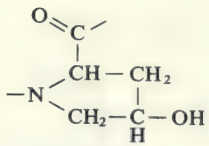
proline



prolyl residue



hydroxyproline



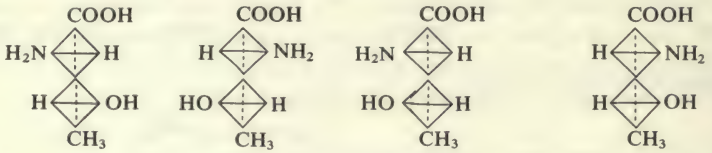
hydroxyprolyl residue

Other amino acids were reported or isolated (*1*) by various investigators. Their existence has, as yet, however, not been fully confirmed as having come from a protein structure.

The amino acids, containing both amino and carboxyl groups, can act in solution as both acids and bases. One must keep track, therefore, of the amphoteric nature of amino acids in order to follow their chemical properties. So it becomes apparent that amino acids must exist predominantly, at least in aqueous solutions, as zwitterions. The term *dipolar ampholyte* is sometimes

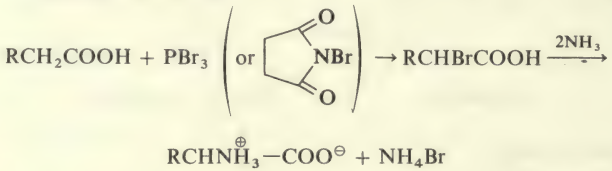
applied. Also, the form in which they carry no net positive or negative charges (isoelectric form) in water solution is almost nonexistent.

In addition, some amino acids, such as cystine, threonine, isoleucine, and hydroxyproline contain two asymmetric carbon atoms. This means that there are four forms of each, as in threonine,



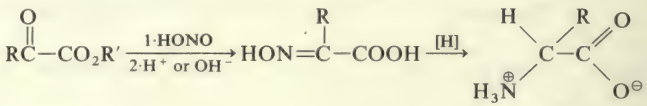
21-1. Synthesis of Amino Acids

α-Halogen acid synthesis. This synthesis is based on halogen replacement of α carbon, followed by amination,

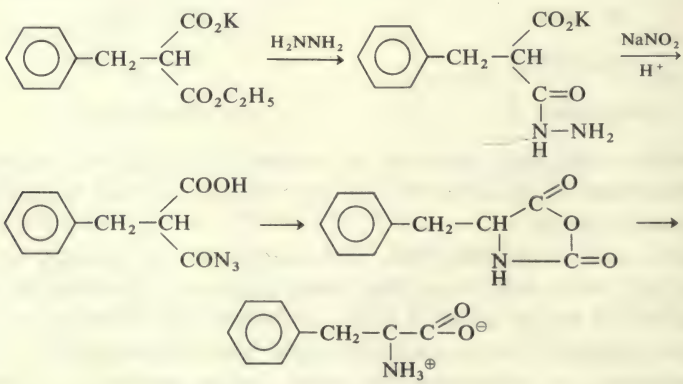


Malonic acid synthesis can also be conveniently employed in this instance.

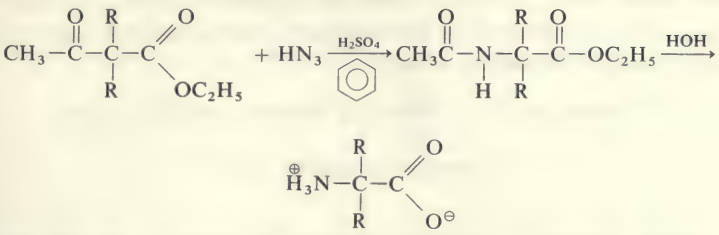
Reduction of α-oximo acids:



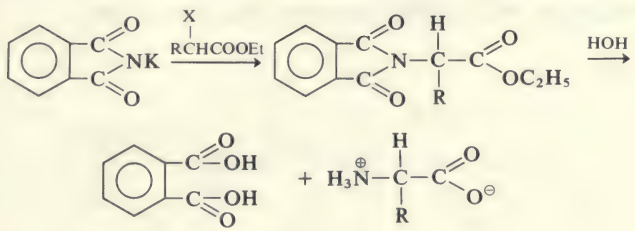
By means of the Curtius reaction:



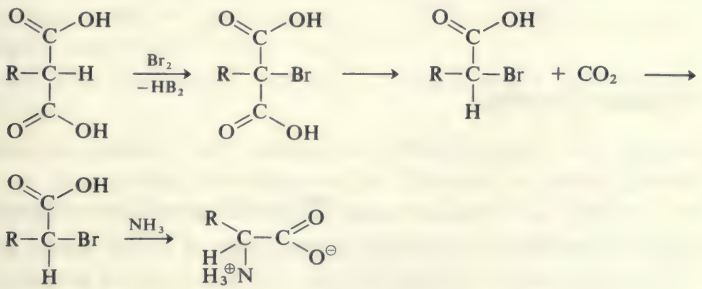
By means of the Schmidt reaction:



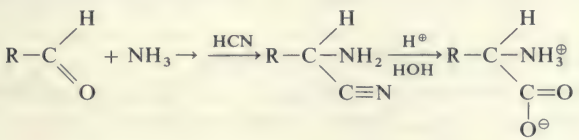
Gabriel amino acid synthesis:



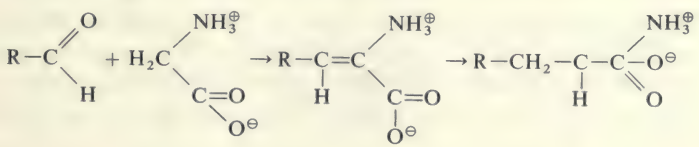
From derivatives of malonic acid:



Strecker amino acid synthesis:



Aldehyde condensations with glycine derivatives:

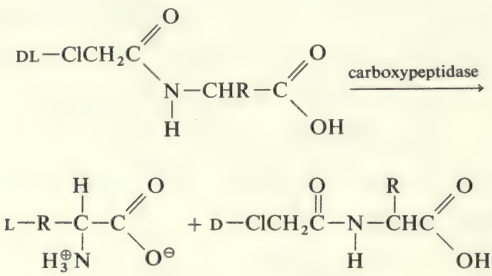


Resolution. All synthetic methods mentioned above lead to racemie mixtures. As a result, separation into desired isomers is often required. This can be done by forming *diastereoisomers*, or *diastereomers*, through combining them with one optical form, for example, a base,

$$\text{DL-amino acid} + \text{L-base} \rightarrow \text{L-base} - \text{D-amino acidate}$$

$$+ \text{L-base} - \text{L-amino acidate}$$

The reaction introduces a second center of asymmetry, making separation based on different properties possible. Alkaloids such as brucine and strychnine are quite useful for such purposes. Enzymes have also been employed for such separations as they will usually only react with the L form,

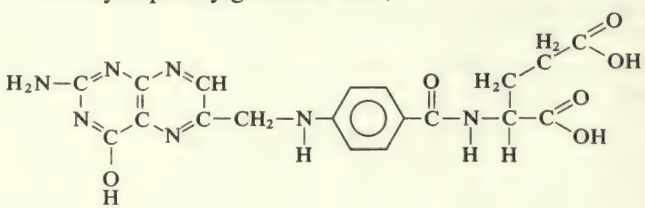


21-2. Oligomers (Peptides)

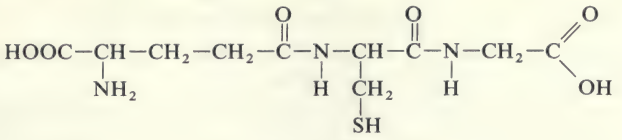
Even though the high polymeric substances, the proteins, are common in nature, the oligomers, or naturally occurring dimers and trimers, etc., are also abundant. The range in molecular weight at which one refers to them as peptides or as proteins is not clear. An arbitrary maximum of 10,000 seems to be often used. The smallest known peptides are dimers, which would contain only one peptide link. The number of amide linkages is often used as the means for designation. Thus a tripeptide means that the molecule possesses three amide links, and so on.

Some of the better known peptides are as follows.

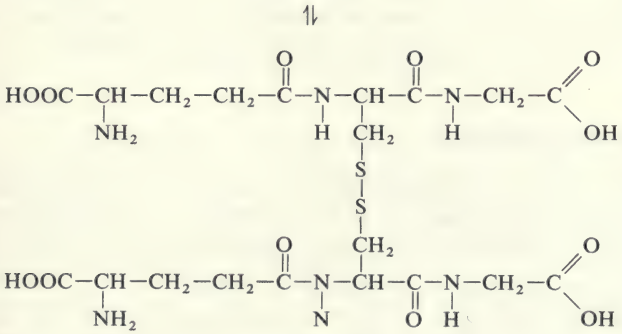
Folic acids. These vitamins are a family of derivative of L-glutamic acid. They are growth factors and to a limited extent antianemia factors. The progenitor of the family is pteroylglutamic acid,



Glulathione. This is a tripeptide found in yeasts and in mammalian blood,



reduced form



oxidized form

Gramacidine. This compound contains 22 amino acid residues in combination with two molecules of ethanolamine. Almost half of the amino acid residues are of D-configuration (D-valine and D-leucine).

Bacitracin. This is a peptide containing D-amino acids. The molecular weight is less than 2000.

21-3. Isolation and Types of Proteins

Pure proteins are only obtainable after many purification steps. This is often possible by using repeated reprecipitation from aqueous solutions. Fractional precipitation with solutions of ammonium sulfate or sodium chloride as well as with acetone or alcohol is also often successfully employed. When a labile material such as an enzyme is being purified, all operations must be conducted below 0°C. Physical methods of purification are also often employed. These are electrophoresis and ultracentrifugation. Pure proteins may then be identified by comparing their properties as well as by studying a mixture for homogeneity.

Much research is still being done on structure elucidation of many proteins. One very good example would be work by Brand and Kassell (*4*), who have determined the structure of β-lactoglobulin in 1945 to be composed of: $(\text{alanine})_{29}$-$(\text{argenine})_{7}$-$(\text{aspargine})_{36}$-$(\text{cysteine})_{4}$-$(\text{cystine})_{8}$-$(\text{glutamic acid})_{24}$-$(\text{glutamine})_{32}$-$(\text{glycine})_{8}$-$(\text{histidine})_{4}$-$(\text{isoleucine})_{27}$-$(\text{tyrosine})_{9}$-$(\text{tryptophan})_{4}$-$(\text{valine})_{21}$.

Although some proteins are composed entirely of amino acids, others have different groups present in their makeup as well. Such proteins are called *conjugated proteins.* The most important ones among these are:

1. *Nucleoproteins.* These are conjugates of protein and nucleic acid, either ribose nucleic acid or deoxyribose nucleic acid.
2. *Chromoproteins.* These contain prosthetic groups consisting of metal atoms surrounded by tetrapyrrole structure (one of the porphyrins).
3. *Glycoproteins.* These contain carbohydrates or carbohydrate derivatives.
4. *Phosphoproteins.* These contain phosphate groups which are presumably esterified with the hydroxy residues of the hydroxyamino acids.

21-4. Structure of Proteins

The determination of structure of proteins has been the subject of many investigations over the last 60 or more years. This included studies on composition, conformation, and functions. Much still remains to be learned, although the record of achievement is very impressive, indeed.

A complete chemical study of structure must not only include an identification of all amino acids present in the structure, but must also identify all other compounds present, should they occur, as well. In addition the proper sequence and quantity of these amino acids in the overall structure must be found.

Furthermore, it is necessary to establish all chemical linkages present. Most investigators accept the peptide linkage theory. Nevertheless, many workers still question the likelihood that all bonds between amino acids in proteins are simple peptide links. At least some evidence appears to exist that some small amount of diketopiperazine linkages, for instance, might be present in some proteins as well. In addition, a disulfide linkage occurs in proteins possessing cystine residues in their makeup. The ester linkages possible in at least such instances as vitamin phosphates, which are known to be significant in enzyme structures (*5*), must also be considered.

Finally, secondary bond forces play a very important part in the steric configuration of protein structures. These are coulombic attractions and repulsions as well as hydrogen bonding. Their nature and magnitude must be determined.

21-5. Configuration of Proteins

It would seem at first that the task of predicting the configuration of a polypeptide chain is too enormous. What helps, however, is that steric restrictions exist. Thus Pauling and Corey (*6*) demonstrated that the amide group has 50% double-bond character and that rotation about it is restricted. As a result, the polyamide chain has almost planar amide groups attached to the bonds connecting the α-carbon atoms (Figure 21-1). Certain combinations of

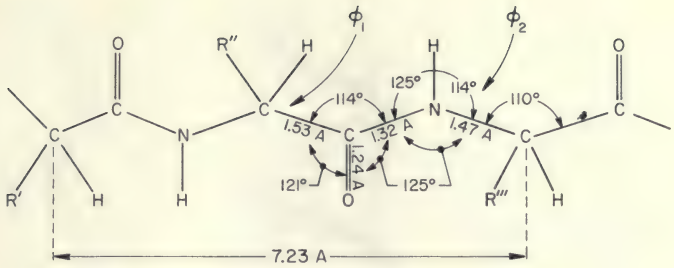


Figure 21-1. Amide link.

angles, ϕ_1 and ϕ_2, will lead to clashes between neighboring atoms in the chain, so that rotation about these bonds is also sterically hindered.

A systematic study was carried out by Liquori (*7*) on all possible variations of the two angles ϕ_1 and ϕ_2. With the use of appropriate functions, the free energy of the chain for all possible angles of ϕ_1 and ϕ_2 was programmed and worked out on a computer. The results yielded only four significant minima. One of these corresponded to a right-handed α-helix originally proposed by Pauling and Corey (*8*). Another was symmetrically related to a left-handed α-helix. A third to a "polyproline" structure and the fourth to a "pleated-sheet" structure.

This α-helix, as suggested by Pauling and Corey (*8*), is based on the assumption that each nitrogen atom forms a hydrogen bond with a carbonyl oxygen atom of another residue, the distance between the hydrogen-bonded nitrogen to oxygen must be not more than 30 degrees from the N—H direction. In the α-helix, each N—H group is hydrogen-bonded to the carbonyl oxygen of the third residue from it. There are 3.7 residues per turn of the helix with the pitch corresponding to 1.5 A per residue. The hydrogen bonds will then run approximately parallel to the fiber axis (Figure 21-2). This structure may be compared to a staircase with the amino acid residues comprising the steps. The height of each step would be 1.5 A, with the height of each turn 5.4 A, so there are 3.6 steps for each turn. As a result, every fifth turn there is an atom located exactly above another.

It is now quite apparent (*9*) that the α-helix of Pauling and Corey (*8*) is the most important configuration of many proteins, such as fibrous proteins and enzymes. The remarkable thing about this proposed structure is the fact that it is also correct for many synthetic polymers.

Although an examination of the α-helix structure might suggest that the configuration is dependent upon hydrogen bonding alone. Liquori's work (*7*) actually demonstrated that other secondary bond forces are involved as well, namely, the van der Waals interactions. This explains why the α-helix formation of proteins also occurs in water solutions, as there hydrogen bonding would be interfered with by water molecules.

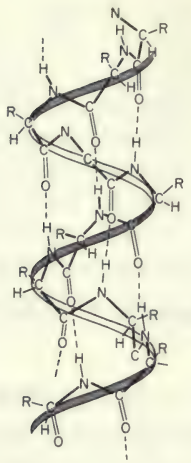


Figure 21-2. α-helix. (Courtesy of Professor L. Pauling.)

The right- and left-handed α-helixes are not stereoisomers but different structures, because in the right-hand helix the side groups are in the *cis* position to the oxygen.

In contrast to the α-helix, some proteins, such as occur in collagen, can take the shape of threefolded helixes.

A third type of protein structure, also suggested by Pauling and Corey, is the "pleated-sheet" structure. Here the molecules are arranged in planar sheets, which as the name implies, are, however, folded or pleated. This structure can actually be of two types. In the first one, all the chains are parallel to each other, and in the second one, antiparallel. In such structures the chains are almost completely extended, forming hydrogen bonds with neighboring chains. The

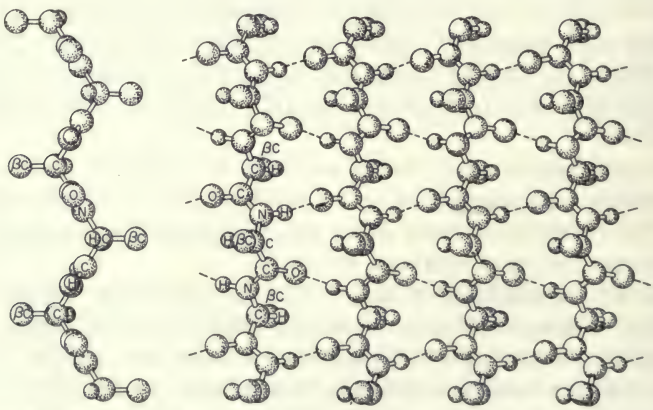


Figure 21-3. Parallel-pleated sheet. H bonds can be seen as being at right angles to the chain direction. (Courtesy of Professor L. Pauling.)

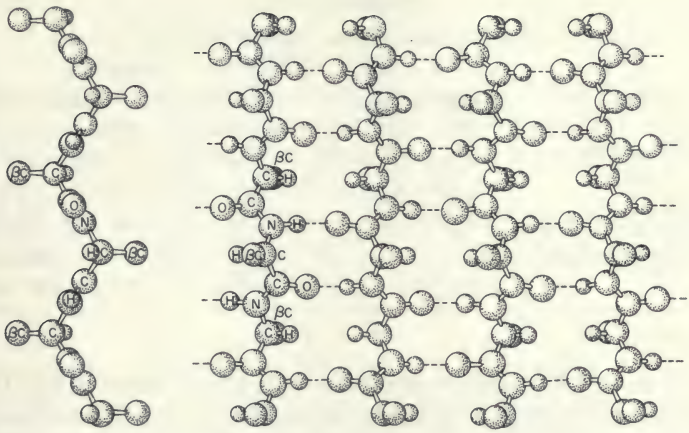


Figure 21-4. Antiparallel chain-pleated sheet. (Courtesy of Professor L. Pauling.)

identity distance of the parallel chain-pleated sheet is 6.5 A, and the antiparallel chain-pleated sheet is 7.0 A. This arrangement is actually very similar to that found in many synthetic polyamides (Chapter 15). This is illustrated in Figures 21-3 and 21-4.

Finally, many proteins, including many physiologically active ones, such as the enzymes which regulate chemical cell reactions, are spherical in structure. These are called *globular proteins.* They are often found to occur naturally in aqueous solutions, such as in plasma, egg white, and milk. The globular structure of these molecules manifests itself in such phenomenon as low viscosity of their solutions, which perhaps could be explained as being due to the absence of chain entanglements. The construction of these proteins might be possible in two ways: (1) they are lateral aggregates of relatively short polypeptide chains, or (2) they are highly folded, large-molecular-weight chains compacted into almost spherical bodies. The latter structure is favored (*1*).

21-6. Chemical Composition of Proteins

Of all the protein structures that occur in nature, only one is known in atomic detail, that of myoglobin, a globular protein. In addition, the composition of one other protein is approximately known, that of hemoglobin.

The knowledge of the sequences in which the amino acids are arranged in proteins started evolving in the early 1930s. This is, however, a very difficult task, and in many cases only the terminal residues are known. In one case, however, that of insulin, which is a smaller-sized polypeptide chain, the structural detail is understood with certainty (*10*).

The first step in determining the composition of proteins consists of proper hydrolysis. Both acids and bases have been employed for this purpose. Enzymes

TABLE 21-1

Molecular Weights of Certain Proteins[a]

Protein	Osmotic pressure	Sedimentation diff.	Sedimentation equilib.
Ribonuclease (enzyme)	15×10^3	12.7×10^3	13×10^3
Zein (corn protein)	39×10^3	40×10^3	—
Egg albumin	45×10^3	44×10^3	40.5×10^3
Horse hemoglobin	67×10^3	68×10^3	68×10^3
Tomato bushy stunt virus	—	$10{,}600 \times 10^3$	$7{,}600 \times 10^3$
Insulin	—	46×10^3	35×10^3

[a] From Reference *16*.

can be used as well. The individual amino acids must then be isolated from the resulting mixture. In the past they were often converted to the methyl ester first and then submitted to fractional distillation. This was then followed by precipitation with special reagents or by fractional crystallization. More recently, chromotographic techniques were shown to be very useful (*11–13*).

The mere identification of the amino acids in a hydrolysate does not, of course, shed light on their sequences in the polymer chains. Some information on this can be obtained by carrying out incomplete hydrolysis and by identifying di-, tri-, and tetrapeptides. In addition, certain enzymes such as carboxypolypeptidase can cause splitting of amino acids from one end of the chain individually. This was used by Lens (*14*) to identify amino acids and their sequence in insulin.

The molecular weight of proteins must also, of course, be established for proper characterization. This was carried out by standard methods on a great variety of proteins (*15*). Some limitations exist on some of these methods by the fact that proteins are generally insoluble in nonpolar solvents. Ultracentrifugation, however, is used extensively for many studies. Table 21-1 shows some molecular weights obtained.

21-7. Some More-Prominant Proteins

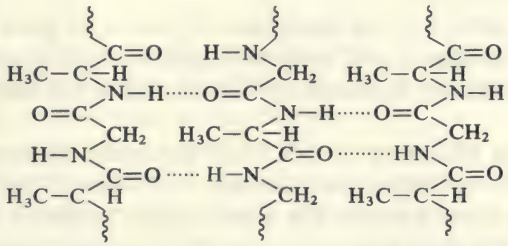
Fibrilar Proteins

The thread spun by the caterpillar of the silk moth, *Bombyx mori*, has a fibrous core, or silk fibrin, which has been utilized for many centuries as a useful fiber. The composition of this protein was studied extensively, although all questions have not as yet been answered. The quantities of all amino acids present were reported by Bergmann and Niemann (*17*) and Abderhalden (*18*). Original X-ray studies by Herzog and Jancke (*19*) and by Brill (*20*) demonstrated that part of silk fibroin is crystalline with the identity period along the fiber axis equal to 7 A with a tentative cell arrangement of four glycine and four alanine units. More details were brought out in subsequent studies (*21–23*). As a result, the information for the unit cell in silk from *Bombyx mori* is $a = 9.65$ A, b(fiber

axis) = 6.95 A, C = 10.4 A, and β = 62.4°. By comparison, silk from *Antheraea mylitta*: a = 9.5 A, b = 6.95 A, C = 11.8 A, and β = 66°. The lattice of silk was interpreted as a primary-valence chain lattice (*1*).

It is believed from interpretation of silk dimensions (*15*) that the chains consist of glycine and alanine residues without strict alternation of the two types of residues. Thus serine could occur in place of alanine, and so on, although large residues such as tyrosine or arginine are unlikely.

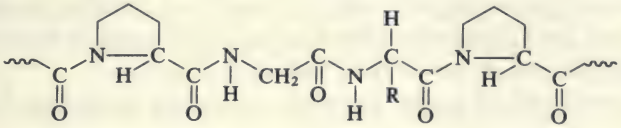
The chains are believed (*23–25*) to be united laterally by hydrogen bonding between CO— and NH— groups and thus form laminae or grids, which are themselves associated by weak secondary valences,



Collagen and Gelatin

Collagen fibers occur in animal skin as well as in connective tissues and elsewhere. When heated in water they gradually transform into a water-soluble substance called *gelatin.* The structural units of gelatin and collagen are well known. The proportions of glycine, proline, and hydroxyproline are high.

Differences between the structural functions of individual members of the collagen group are limited, and their mechanical properties exhibit no large-scale differences such as those which exist between keratin and myosin. Collagen fibers cannot be stretched more than just a few per cent without breaking. This is associated with extended chain configurations,



The chains form a triple helix. Upon heating in water, the helix will break up; then, when cooled, a gel forms, but the molecular weight now is much lower, and the triple helix does not reform. The product is gelatin. Here the spacing increment of collagen (estimated at 10–15 or 17 A) is increased 35%. This could correspond to one or two water molecules between the chains.

Collagen fibers, when immersed in hot water, will contract spontaneously to about one-quarter of original length. This contracted fiber gives amorphous X-ray diffraction pattern.

Keratins

The keratins are found in wool, whale bone, horns, and so on. These are insoluble proteins which swell to a limited extent only and are fairly resistant (by comparison) to hydrolytic action. It is assumed that the amino acids are high in cystine content, which is responsible for the S—S bridges cross-linking the peptide chains (*26–29*). This also explains the sensitivity of keratin toward alkali sulfides that reduce the S—S linkage.

From studies of wool, it was concluded (*15*) that "wool keratin" is not a homogeneous substance. Thus any conclusions about its structure must be approached with caution.

Microscopic studies of the main part of hair and wool fibers, called the *cortex*, reveals spindle-shaped cells with positive and uniaxial birefringence, suggesting an oriented molecular structure. This was later identified as a α-keratin.

From studying stretching of hair when softened with hot water and alkali (*30*) and from X-ray diffraction patterns, it was found that keratin actually exists (*31*) in the α and β forms. The first is a spiral structure and the second an extended sheet. The high reversible extendibility of wool (about 30% compared to 5% for cotton) apparently arises from the fact that it can exist in either of these two forms.

The α-keratin structure is now believed to involve a helical arrangement of polypeptide chains in which about 3.6–3.7 polyamide residues occur per each turn of the helix. Hydrogen bonding holds the adjacent turns together. The β-keratin, on the other hand, consists of nearly extended polypeptide chains arranged in sheets through hydrogen bonding. The sheets are pleated and not quite planar, similar to the structure of silk fibroin, in which every chain is a mirror image of its neighbor. Because there are both crystalline and amorphous regions in hair and wool, it was suggested that some preliminary fiber extension exists, owing to stretching of the nonoriented phase of the fiber.

Two principal types of side linkages appear present: (1) covalent bonds due to the bifunctional cystine moiety, which is capable of bridging to adjacent polypeptide chains, and (2) secondary bond forces, salt linkages, or hydrogen bonding between charged end groups of polar amino acid residues.

The two structures of α- and β-keratin are shown in Figures 21-5 and 21-6.

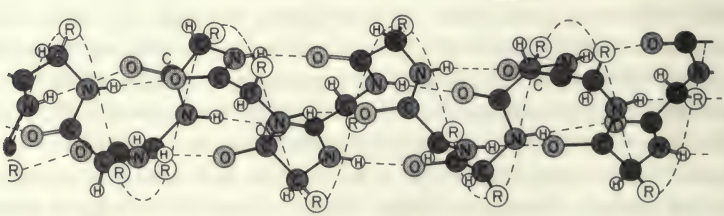


Figure 21-5. α-keratin. (From Reference *16*.)

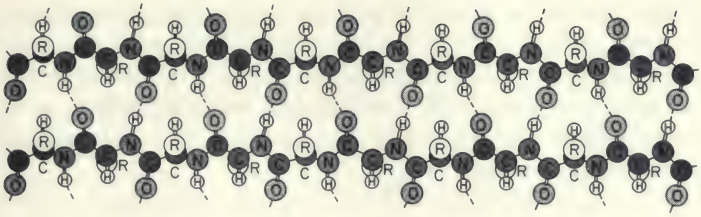


Figure 21-6. β-keratin. (From Reference *16*.)

Globular Proteins

These polymers differ from the previously mentioned proteins by being particles possessing compact shapes. These shapes may either be spherical or they may depart from truly spherical structures.

Many, if perhaps not all, proteins of this type may be transformed into fibrous proteins by certain denaturating chemicals such as urea or formamide. As these reagents should only be capable of interfering with secondary bond forces, it appears quite likely that globular proteins hold their shape because of secondary bond forces such as hydrogen bonds. The only classification available for these proteins is based on their solubilities: (1) albumins, which are soluble in salt-free water; (2) globulins, which are soluble in appropriate salt solutions in water but insoluble in ion-free water; and (3) prolamins, which are soluble in dilute alcohol.

Enzymes

Enzymes are biological catalysts. Their function in nature is to increase the reaction rates in organisms or living systems, where they can be found universally. It is likely that most biological reactions are enzyme-controlled. It is also very significant that enzymes allow many complex reactions to take place at organism temperatures, which under artificial circumstances would require far higher temperatures. Many of the enzymes are simple proteins. Others are conjugated proteins containing prosthetic groups. Here these groups are known as *coenzymes.*

It appears that those enzymes which are simple proteins are primarily hydrolytic in their actions, whereas those which are conjugated possess mainly nonhydrolytic catalytic function. The mechanism of enzyme action is much more specific than that encountered from nonbiological catalysts.

Two extreme types of catalyzed reaction are recognized in chemistry: homogeneous and heterogeneous, depending on whether the catalyst can be considered as existing within the same phase as the substrate or as a separate phase. In the first case, catalysis is assumed to result from the formation of an intermediate compound or complex between reactant and catalyst. In the second, the reactants are presumed to be absorbed on the surface of the catalyst.

Enzyme action might be described perhaps as a case of intermediate between the two extremes, having some of the character of both. Although enzymes are usually considered as existing in true solution, the bulk of these molecules forces them to occupy specific surfaces. Nevertheless, most investigators appear to agree that direct combination between enzyme and its substrate appears to be a necessary prelude to reaction.

21-8. Denaturation of Proteins

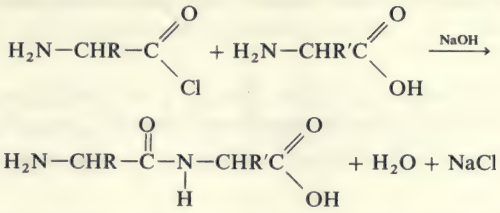
As a result of harsh treatment, soluble proteins can undergo profound structural changes. This results in changes in solubility that often result in coagulation as well as in loss of specific biological activity. Simultaneously, solution viscosity changes and the ability to crystallize is lost. This is known as *denaturation.* Such harsh treatment can be mechanical, or it can be caused by heat, organic solvents, or electrolytes. The sensitivity of proteins toward such influences vary and it appears possible (*15*) that in spite of superficial similarity, various types of denaturations are dependent upon the treatments used. Reversibility of denaturation was observed in several cases (*31,32*).

Although the mechanism of denaturation has received much attention, not all points are as yet fully elucidated. Several studies indicated that denaturation is primarily an unraveling process, where the folded form, a *globulus,* unfolds or else the chains fold into another or different manner. This is supported by a number of observations, such as higher viscosity of denatured products, and the Astbury and Lomax observation (*33*) that many proteins yield an X-ray diagram similar to silk or β-keratin after denaturation. Also, unfolding of a regularly folded peptide chain would explain the fact that individual groups become detectable which were previously undetectable and apparently hidden in the interior of the molecule. The change in solubility can also be explained on this basis of the assumption that in the natural protein the hydrophobic groups are folded into the interior of the molecule and the hydrophilic groups are on the exterior capable of interaction with water molecules at the surface. All these explanations, however, neglect the findings of Wu and Lee (*34,35*) that the properties of a denatured protein depend to quite an extent upon the method of denaturation.

21-9. Synthesis of Polypeptides

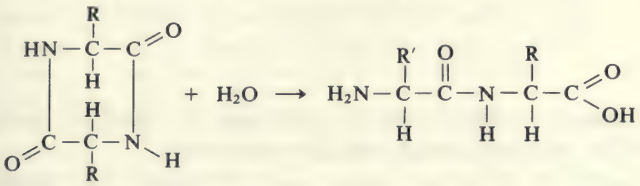
Structure-elucidation studies of proteins as well as the need for their better understanding created the necessity for synthetic approaches to polypeptides. As a result, many investigations were conducted into possible peptide syntheses. Some of the more common approaches utilize the following reactions:

Aminoacyl halide reaction (*36*):

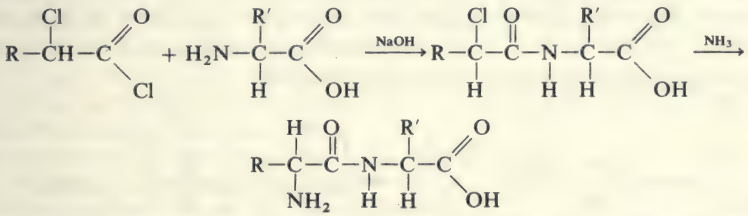


The stability of the acid chloride can be a problem in this reaction. Self-condensation of the acid chloride would also be a drawback.

Diketopiperazine hydrolysis. This method is based on the ability to hydrolize one of the peptide linkages at a faster rate than the other. The method is actually limited to dipeptides from a single amino acid,

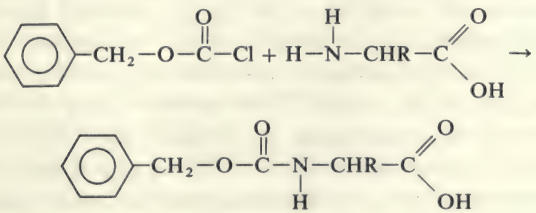


Haloacyl halide method (*36*),

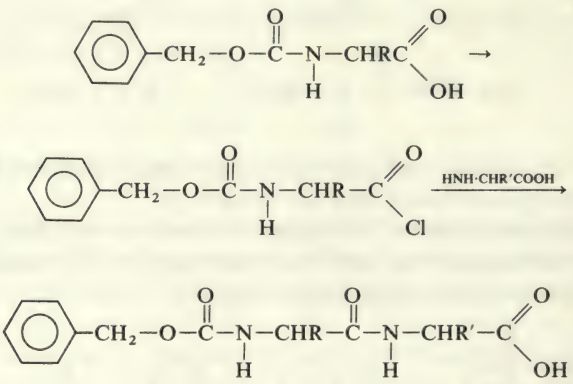


This method has been used for synthesis of many peptides, although its disadvantage is the inability to employ optically active intermediates. Nevertheless, this method afforded the syntheses of relatively large polypeptides.

The *Bergmann–Zervas carbobenzoxy method* (*37,38*) employs a blocking group (benzyloxy carbonyl) which combines with optically active amino acids, but which can be subsequently removed from the penultimate unit of the product by nonhydrolytic means. The condensation with the amino acid is a Schotten–Bauman reaction,

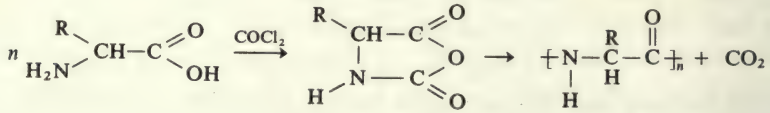


Subsequent conversions of the acid to the corresponding acid chloride followed by a Schotten–Bauman reaction with an amino acid permits peptide formation,



The carbobenzoxy residue may be removed by catalytic hydrogenolysis, yielding the desired peptide and volatile byproducts.

Polymerization of N-carboxy amino acid anhydride. This method (as was shown in Chapter 15) leads to high-molecular-weight condensates of α-amino acids. Actually earliest work, by Leuchs (*39*), led to only low-molecular-weight condensates. Recently, however, polymerizations to molecular weight as high as 100,000–1,500,000 were shown to be possible through use of tertiary amines and other strong bases to catalize the reaction (*40*),



As far as is known, use of strong bases not only permits attainment of high molecular weights, but also allows us to carry out reactions without racemization. Many polypeptides were synthesized with the aid of this reaction. Kinetic results indicate that effective initiators might actually be low-molecular-weight adducts rather than strong bases, with the polymerization perhaps involving an electron-transfer mechanism (*41*).

Copolymerization of α-amino acids by this method can be carried out, but random copolymers are only possible under very special conditions, as the rates of addition of each monomeric species to the growing peptide chain must be equal regardless of the nature of the terminal unit. So the possibility of obtaining truly random copolymers, particularly when more than two amino acids are involved, appears quite slim (*42*). Block copolymerization is possible by employing preformed polypeptides containing free amino groups as initiators.

The desired synthesis, of course, would be one permitting controlled sequences for synthetic polypeptides. This would permit relating chemical composition with macromolecular structures and with biological functions in proteins.

Work along these lines is in progress, with the success to date being limited to relatively small polypeptides. One noteworthy example of this is work by Hofmann and Yajima, who reported the preparation of a tricosapeptide amide (*43*).

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Polynucleotides

22

Two major classes of macromolecules underlie the functioning of living organisms. These are proteins and nucleic acids. The proteins are more familiar to us. This is so, because biochemists have, over the last 20–30 years, established complete sequences of amino acids in a few proteins and know many points about the composition of others (see Chapter 21). Nucleic acids, on the other hand, are much less well known. Amazingly enough, this is in spite of the fact that they were actually discovered as early as 1869, but they received little attention until 1944.

Two types of nucleic acids are known: deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). DNA occurs in the cell nucleus of plants and animals. RNA occurs in both the cell nucleus and in the cytoplasm.

In nature, nucleic acids are bonded to highly basic protamines to form nucleoproteins. The exact nature of this bond is not too well understood (*1*).

The best known nucleic acids are the thymonucleic acid obtained from thymus and the yeast nucleic acid. Nevertheless, many other nucleic acids have now been isolated from a number of divergent sources, such as cancer tissues, chick embryos, nitrogen-fixing bacteria, wheat germ, tubercle bacilli, and so on.

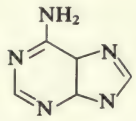
Doty (*2*) suggested that the function of DNA is to act as a store house of genetic information which RNA transmits to the centers of metabolism. The information is passed from generation to generation by means of self-replication of DNA. This information is furthermore imprinted on RNA during RNA synthesis and thereby transmitted further to proteins.

To understand the genetic code, it became fundamentally necessary to elucidate the structure of nucleic acids. As a result, the composition of different DNA strands is now being studied (*3*). At present, the sequence of the bases within the molecules still remains by and large a mystery. Upon acid hydrolysis, nucleic acids yield (1) phosphoric acid, (2) purine and pyrimidine bases, and (3) pentoses.

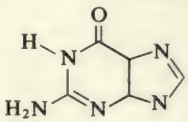
It is now also known that nucleic acids are essentially linear copolymers, all consisting of mostly the same structural plan but differing in the nature of individual carbohydrates and bases.

DNA molecules make use of five different bases in their composition: guanine, cytosine, thymine, 5-methyl cytosine, and adenine. RNA molecules, on the other hand, contain only four bases—adenine, guanine, cytosine, and uracil. The structures of these bases are as follows:

Purines:

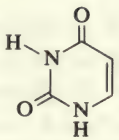


adenine

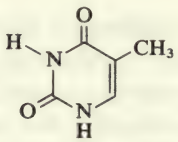


guanine

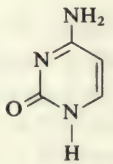
Pyrimidines:



uracil



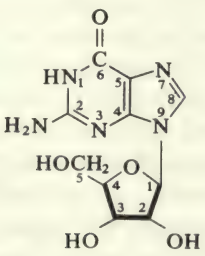
thymine



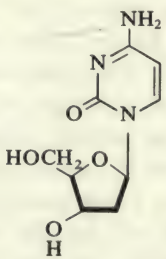
cytosine

Other trace purines were found in nucleic acids, but these are all methyl derivatives (usually N-methyl) of guanine and adenine. It is interesting that thymene is found only in DNA molecules, whereas cytosine is found in both DNA and RNA. The ratio of adenine to thymine and that of guanine to cytosine appears to be very close to 1.

Nucleosides are pentose derivatives of purines or pyrimidines. These are the building blocks in nucleic acids. D-ribose is the pentose found in RNA and D-2-deoxyribose is the pentose found in DNA. In both nucleosides, the linkages occur from the 1 position on the β-D-furanoside to the 9 position of purines and the 1 positions of the pyrimidines,



guanosine

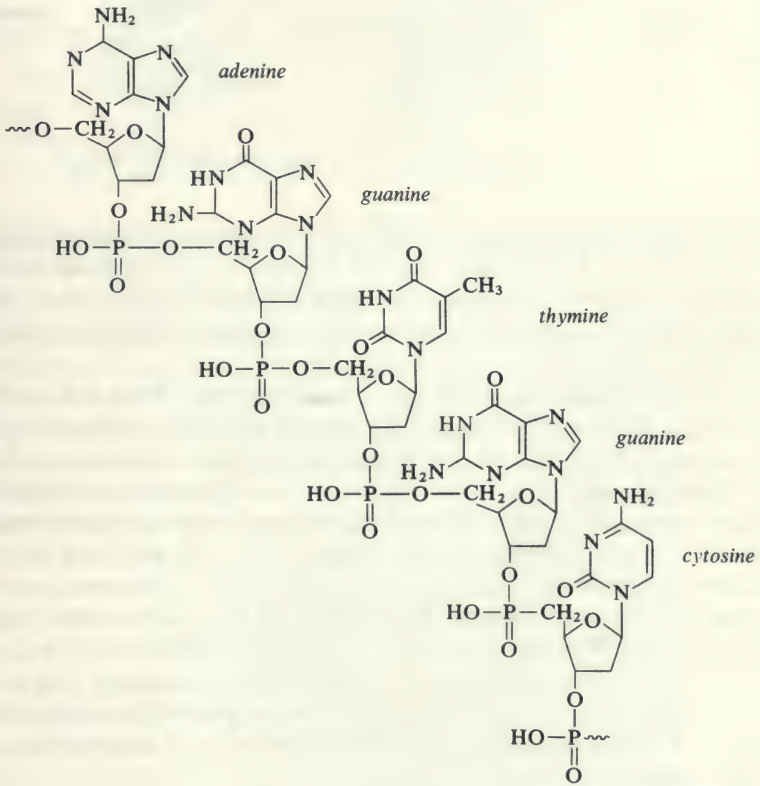


deoxycytosine

Nucleotides are phosphate esters of nucleosides. The phosphate moiety may occur on any one of the hydroxyl positions or may even be a cyclic phosphate in the case of RNA nucleotides. Hydrolytic or enzymatic cleavage of a nucleic acid may result in a 3- or 5-phosphate, or both, depending on type of enzyme used or on the method of hydrolysis. As a result, considerable evidence has been compiled that the linkages of the nucleotides leading to polynucleotides occur at the 3 and 5 positions.

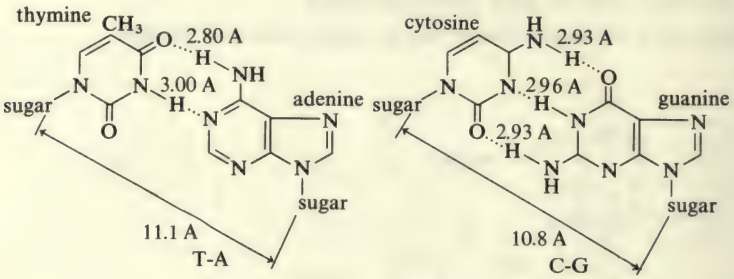
Most methods of nucleotide analyses are based on chromatography or electrophoresis of the products from hydrolysis. Schildkraut et al. (*4*) introduced a technique of analysis based on measuring the buoyant density of DNA in cesium chloride. This density was found to be proportional to the molar per cent of guanine plus cytosine content in the nucleic acids. Small quantities of material are sufficient for such determinations.

A segment of a DNA molecule can be illustrated as follows:



A similar illustration can be made for a segment of an RNA molecule. The sequence of nucleotide units probably varies with different nucleic acids, each having its peculiar combination. It is known, however, that in DNA molecules,

the ratio of adenine to thymine and that of guanine to cytosine are nearly always 1:1. This, plus information obtained with X-ray diffraction studies (*5*), lead to a proposed three-dimensional structure for the DNA molecules to be a double helix, consisting of two chains side by side and twisted together (*6*). The purine or pyrimidine moieties are so arranged that they suit geometric requirements for hydrogen bonding through the core of the double helix. This allows for two purine-to-pyrimidine pairs, adenine to thymine and guanine to cytosine, to have hydrogen bonding in the helix. Each of the four bases can occur in either one of the chains, and the pairing must occur from the opposite direction in the corresponding chain. So there can be four possible pairings; cytosine-guanine, guanine-cytosine, thymine-adenine, and adenine-thymine. Looking down the core of the helix, the pairings can be represented as follows:



Such a model for DNA was proposed by Watson and Crick (*6*) and now bears their name, the Watson–Crick model (Figure 22-1). As is shown, the two chains are coiled in a right-handed helix about a common axis, and, as the two base pairs are approximately equal in size, the sugar phosphate can assume a regular conformation.

Some modifications were introduced into the Watson–Crick model by Wilkins and co-workers after they carried out X-ray diffraction analyses on Li salts of DNA (*7–9*). In the Wilkins model, the conformation of the nucleic acid depends upon the counterion present as well as upon the relative humidity of the fiber environment. Depending on conditions, three conformations were actually observed. These were labeled A, B, and C. All three are helical and assume the Watson–Crick base pairing. They differ, however, from each other in the helix pitch, conformation of the nucleotides, and the number of nucleotide pairs per turn of the helix. These are 11 for A, 10 for B, and 9.3 for C.

An X-ray diffraction study of sodium DNA (*1*), combined with steric studies, led to the elimination of left-handed coiling of the helix as a possible structure for the A conformation. It is also believed that the B conformation assumes a right-handed helix (*10*).

X-ray diffraction patterns of DNA molecules from spermheads (*11*), chromosomes (*12*), and T2 bacteriophage (*13*) indicated B conformation. This conformation appears to be true also for the high-humidity form of all DNA salts and for DNA in solution (*14*). As a result, it is believed that the B conformation

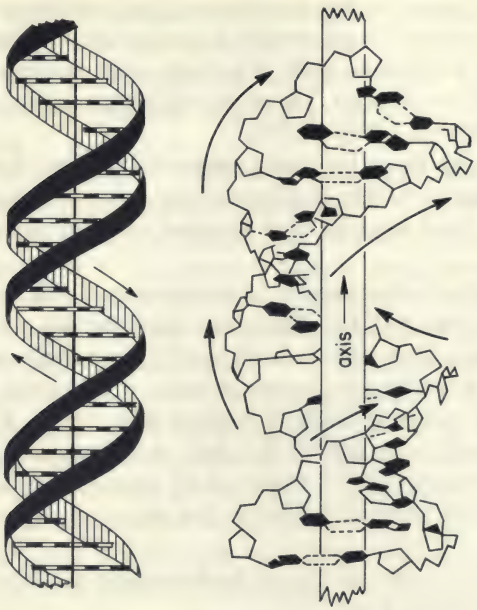


Figure 22-1. Illustration of the Watson–Crick model.

is the biologically important one and that the A and C conformations are shapes assumed as result of drying.

Langridge and Rich (*15*) carried out X-ray diffraction studies on synthetic polynucleotides. Their results raised the question about the cytosine residue actually existing in the amino form, as proposed by Watson and Crick (*6*) or rather in the imino form. In addition, Donahue and Trueblood (*16*) pointed out that on the basis of calculated dimensions, an adenine-guanine pair could exist and would fit in the Watson–Crick helix. Furthermore, Hoogsteen (*17*) observed that although in the mixed crystal of 3-methyl thymene and 9-methyl adenine, the bases are hydrogen-bonded together into pairs, the bonding pattern is different from the one assumed by Watson and Crick.

On the basis of further X-ray studies (*18,19*), Wilkins and co-workers offered a DNA model with very regular molecular conformation in which the glycoside links of the four base pairs occupy equivalent positions (*19*). This model is approximated by the Watson–Crick model.

Wilkins feels (*20*) that the structure of DNA is now fairly well established. The sequences of the bases in the molecules appear to determine their functions. Recent studies by Gatlin and Davis (*21*) demonstrated an apparent correlation between per cent amino acid in protein and per cent cytosine-guanine in DNA.

In the natural form the DNA molecule is an anion in which each phosphate group bears a negative charge. It has been demonstrated that DNA molecules are apparently the crucial constituents of the nucleus, carrying in their structure

(in the sequence of bases) the key to inherited characteristics of each organism. This suggests that each cell must contain a number of DNA molecules and that, furthermore, each individual high organism must possess a rather unique combination of DNA molecules. The molecular weight of these DNA molecules ranges from 4,000,000 to 7,000,000 (*22*).

RNA molecules, on the other hand, apparently do not have the distinctive base pairing peculiar to DNA. It is interesting, however, that RNA molecules contain a ratio of total adenine plus cytosine to total guanine plus uracil of nearly 1.

Also the RNA molecules appear to be smaller than DNA. A typical molecular weight may be 150,000–500,000. The lower figure would correspond to about 500 nucleotide resides. Doty and co-workers (*22*) presented some evidence which indicates that RNA molecules possess secondary structures which are helical regions embedded within a single polynucleotide chain. Furthermore, they observed that actually over half of the chain length assumes this shape. This was confirmed by others (*23–25*). Fresco et al. later offered an explanation (*26*) for the factors which probably govern the development of this secondary structure.

1. Intramolecular interactions cause the formation of the secondary structure which takes the DNA-like form.
2. Within the helical regions base pairs are only adenine–uracil and guanine–cytosine.
3. Maximum pairing takes place because of the ability of nonbonded residues to "loop" out of the helical region, allowing the complimentary residues to fall into place.

The full role nucleic acids play in organisms is now becoming understood as well. Most opinions agree that they function in protein biosynthesis. This can be described very briefly as follows.

Before amino acids are capable of combining into polypeptides in the biological reactions, they undergo a combination, or what is referred to as *activation* (*27*). What it means is that they combine with a specific enzyme and a molecule of a nucleotide, adenosine triphosphate, which serves as a source of energy.

Step 1:

$$\text{Amino acid} + \text{adenosine triphosphate} + \text{enzyme} \rightarrow$$
$$\text{amino acid}\sim\text{adenosine monophosphate}\sim\text{enzyme (complex)} + \text{inorganic pyrophosphate}$$

The activated amino acid is then picked up by a specific amino acid acceptor or transfer RNA (mol. wt. about 25,000). Ochoa points out (*27*) that there are as many specific amino acid enzymes and specific transfer RNA's as there are different amino acids found in proteins.

Step 2:

$$\text{Amino acid}\sim\text{adenosine monophosphate}\sim\text{enzyme (complex)} + \text{sRNA} \rightarrow$$
$$\text{amino acid} - \text{sRNA} + \text{adenosine monophosphate} + \text{enzyme}$$

In this second step, the amino acid is esterified through its carboxyl group with a hydroxyl group of the terminal adenosine moiety of transfer RNA resulting in the release of the nucleoside and the enzyme. The reaction product is then transferred to ribosomes, which are the places of assembly for the polypeptide chains.

As already stated, the sequence in which the amino acids are now linked in the synthesis of polypeptides is genetically controlled. The chromosomal DNA, the bearer of the genetic code, directs the formation of a messenger RNA, which in its composition or sequence of bases is complementary to the DNA. Here another enzyme, RNA-polymerase, catalyzes this reaction.

Ochoa (*27*) states very aptly that the specific sequence of the stepwise assembly of amino acids on the RNA template may be considered a translation of a 4-character language of nucleic acids into the 20-character language of proteins.

The size of the template RNA apparently determines the size of the resultant polypeptide chains. Presently available information indicates (*27*) that the mean molecular weight of messenger RNA is approximately 150,000. It is believed that three nucleotides are required per each amino acid. This would correspond to 170 amino acids or a polypeptide chain of 25,000 molecular weight. This means that only protein subunits are formed on ribosomes which must subsequently polymerize, perhaps in an appropriate ionic environment (*27*).

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Part VI

REACTIONS OF POLYMERS

Graft and Block Copolymers

23

It is often required that a polymer possess a number of diverse properties. Such diverse properties may not be easily achieved by the syntheses of homopolymers alone, so the organic chemist might turn to formation of copolymers or even terpolymers to achieve desired results. But even there the opportunities are limited in what may be realized in terms of physical or chemical properties. Formation of graft or block copolymers with sufficiently long polymeric sequences of diverse chemical compositions sometimes opens the way to meeting more specialized requirements. Thus one might be able to combine the heat resistance of phenolic resins with the elasticity of rubber, or hydrophillic with hydrophobic properties, or properties of crystalline and amorphous polymers.

Various methods of preparation of graft and block copolymers have been described in the literature. These include both chemical and physical means. This chapter will concern itself only with chemical means of preparation. The subject of graft and block copolymers was described thoroughly in two books (*1*,*2*).

A graft copolymer (Chapter 2) is composed of a macromolecular backbone to which are attached at intervals branches of a different macromolecular species. The backbone may be either homopolymeric or copolymeric with pendant groups of either type.

A block copolymer (Chapter 2) is composed of relatively long chains of a certain chemical composition. These chains are separated by either another polymer of a different composition which combines them or by a low-molecular-weight "coupling" group.

Also, the synthetic method used may often determine the molecular structure or the homogeneity of the resultant material even in cases where the same starting materials were used. No general agreement exists, as yet, on the nomenclature to be used for graft and block copolymers (*2–4*). For convenience,

and because of this writer's preference, the nomenclature mentioned in Chapter 1 will be followed.

Most preparative techniques for graft and block copolymers result in mixtures of reaction products and often starting materials. Means must, therefore, be found for separation. Techniques such as fractional precipitation, selective extraction, and selective precipitation are often employed. Chromatography and ultracentrifugation can also be very useful.

23-1. Properties of Graft and Block Copolymers

The behavior of these materials in solution depends very much upon their composition. The differences in polarities of the two or more polymer species making up each molecule often result in unusual solvent effects. Sometimes resistance can be improved by grafting, say acrylonitrile to silicone rubbers (*5*), or the polymers may be made more soluble, as in the case of block copolymer formation of styrene–methyl methacrylate (*6*). Thus block copolymers with less than 10% styrene will dissolve fully in acetonitrile, a solvent for poly(methyl methacrylate) but not for polystyrene. As the quantity of styrene is increased in the copolymer, only partial solubility can be attained. The insoluble portion, curiously enough, is also insoluble in cyclohexane, a solvent for polystyrene but not for poly(methyl methacrylate).

It was observed (*7*) that block copolymers of styrene with methyl methacrylate or with vinyl acetate exhibit lower intrinsic viscosities in toluene than do homopolymers of equivalent molecular weight. This was explained by suggesting that such block copolymers would probably be less solvated and as a result more tightly coiled in solution than would styrene homopolymers, for which toluene is a good solvent.

Miller and Ranhut observed (*8*) that acid strength of homopolymers and copolymers of acrylic acid with acrylamide in water solutions containing sodium chloride decreases in this order: random copolymers > block copolymers ≈ linear acrylic acid homopolymers > branched acrylic acid homopolymers ≈ graft copolymers.

Danon and co-workers (*9*) suggested that in some cases, where a graft copolymer consists of two segments which are completely incompatible, the copolymers composed of intermediate degree of grafting should be insoluble in just about any solvent.

It was also noted in a number of studies (*10–14*) that both graft and block copolymers will often exhibit T_g's similar to those found for blends of corresponding homopolymers. In some cases, the glass-transition temperatures of graft and block copolymers were actually found to lie between the T_g's of their corresponding homopolymers (*15–18*).

Grafting can significantly affect mechanical properties of polymers, such as their tensile and impact strength, extensibility, and so on. Such physical

properties of the copolymers were in some studies found to correspond to physical mixtures of homopolymers (*11*, *14*).

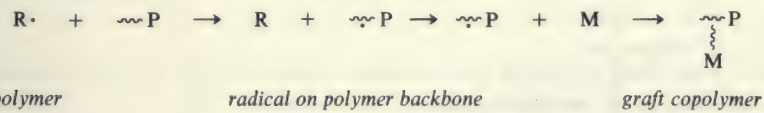
When grafting is carried out on a crystalline polymer and the crystallinity disrupted, the strength of the material may decrease, even though the grafted material may act to reinforce the structure (*19*, *20*). When, however, the crystallization is not interfered with, then continuous increase in strength can be observed with increase of the graft content (*20*, *21*).

23-2. Synthesis of Graft and Block Copolymers

Free-Radical Chain-Transferring Technique

This technique consists of carrying out free-radical polymerization of a monomer (B) in the presence of a preformed polymer from a different monomer (A). During the grafting reaction, an active site, capable of initiating block and graft copolymers, must be formed on the polymer backbone by a chain-transferring step through abstraction of some labile atom. Often, but not always, such an atom is hydrogen.

Actually, though, the growing radical chain is capable of abstracting an atom from any available source in the reaction system. Such a source can be the solvent, or the initiator, or the polymer. So it should be realized that the process is not very efficient and depends upon the presence of labile atoms on the polymer backbone. The grafting process itself can be illustrated as follows:



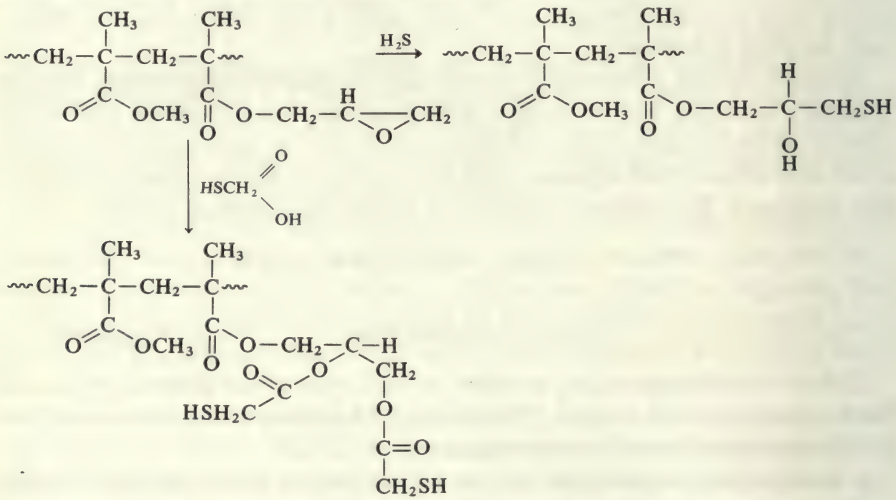
If chain transferring occurs at either or both ends of the polymer, only then block copolymers are formed. The efficiency of grafting based on this method is dependent upon several competing reactions (*22–25*):

1. Competition between the various species present in the reaction mixture, such as monomer, solvent, and backbone for the growing polymer radical. This means that there is competition between chain growth and various chain-transferring steps.
2. Competition for the initiator radical between monomer and backbone.
3. Competition among the terminating processes, such as disproportionation after the polymer radical has formed.
4. Competition among the terminating processes in the growing graft species. If termination occurs through recombination, it should lower the grafting efficiency. But even though the efficiency of this process is low, it has received considerable use because the reactions are quite easily carried out. One needs merely to conduct polymerization of the monomer in the presence of the backbone polymer and a proper free-radical initiator. A solvent may or may not be present. Emulsion systems have been utilized as well. Here the effectiveness of

chain transferring may be a function of the experimental technique, such as rate of stirring, and other factors which may affect the diffusion process. Table 23-1 lists some of the graft and block copolymers formed by the chain-transferring reaction.

Evidence was presented that addition to the reaction mixture of a good chain-transferring agent like a mercaptan (*35*) or CCl_4 or CH_3I (*36*) causes reduction in grafting efficiency. In addition, grafting efficiency is temperature-dependent. This is actually in good agreement with known mechanism for chain transferring (*2*). Also, the efficiency generally tends to increase with the increase in initiator concentration (*1*).

One way to increase the efficiency of grafting was shown by interesting studies of Fox and co-workers (*24*) and of Gluckman and co-workers (*25*). They reacted pendant epoxide groups of methyl methacrylate–glycidyl methacrylate copolymers with hydrogen sulfide or with thioglycolic acid to form mercaptan groups or chain-transferring agents right on the backbones:



When styrene and acrylic or methacrylic esters were then polymerized in the presence of such backbones, the grafting reactions were highly efficient, yielding relatively pure graft copolymers.

The picture is somewhat confusing when it comes to finding the optimum ratio of monomer to polymer. Both Hayes (*35*) and Berlin et al. (*36*) found that the efficiency increased with the increase in the ratio of monomer to polymer in emulsion systems, but decreased for reactions carried out in solution (*1*).

The nature of the initiating radical appears to bear a strong influence on the efficiency of grafting. Thus Smets and co-workers (*41*) found that when methyl methacrylate was polymerized in the presence of polystyrene initiated with benzoyl peroxide, appreciable amounts of grafting took place. When, however, the same reaction was initiated with azobisisobutyronitrile or with ditertiary butyl peroxide, the amount of grafting was insignificant. This can be explained

TABLE 23-1

Some Graft and Block Copolymer Synthesized by the Free-Radical Chain-Transferring Process

Backbone	Monomer	Ref.
Polyacrylamide	Acrylic acid	*18*
	Acrylamide	*26*
	Acrylonitrile	*26*
Polyacrylonitrile	Acrylamide	*8*
Poly(acrylic acid)	2-Vinyl pyridine	*27*
Poly(methyl acrylate)	*p*-chlorostyrene	*28,29*
Poly(methyl methacrylate)	Vinyl acetate	*30*
	Vinyl chloride	*30*
	Acrylonitrile (block copolymer)	*31,32*
	Butyl methacrylate, lauryl methacrylate, and ethyl acrylate	*24,25*
Poly(ethyl acrylate)	2-Vinyl pyridine	*27*
Poly(ethyl-α-chloroacrylate)	Vinyl acetate	*33*
Poly(vinyl acetate)	Ethylene	*34*
Poly(vinyl chloride)	Styrene, vinyl acetate	*35*
	Mixture of butyl methacrylate and methacrylic acid	*36,37*
	Glycidyl methacrylate	*38*
Deoxythioethyl cellulose	Styrene	*39*
Dextran	Vinyl pyrrolidone	*40*

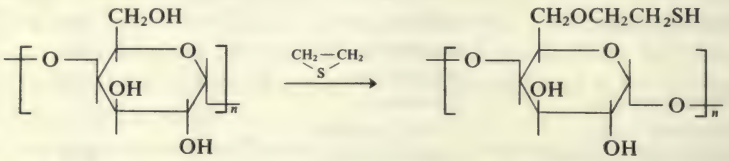
(*41*) on the basis of relative reactivities of the initiating radicals. The less reactive $(CH_3)_2-\dot{C}-C\equiv N$ radical is capable of initiating polymerizations but not capable of chain transferring to the backbone. Such an explanation presupposes that most of the chain transferring to the backbone comes from the initiating radical and not from the growing chains. Studies conducted with polymerization of vinyl acetate in the presence of poly(methyl methacrylate) actually yielded contradictory results (*41*), indicating that the efficiency of grafting in this case was independent of the initiator. All this leads to the conclusion that not only the reactivity of the initiating radical must be considered, but also the nature of the backbone and the reactivity of the growing chain radical.

Last, the reactivity of the radical on the backbone toward the monomer may also have a bearing on the efficiency of grafting. Smets and Claesen (*30*), for instance, found that they could not graft vinyl acetate to polystyrene and methyl methacrylate to poly(vinyl acetate) or poly(vinyl chloride) efficiently.

Polymer with Reactive Sites for Chain Transferring

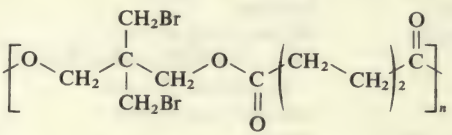
The low efficiency of the grafting reaction has resulted in a number of efforts to synthesize backbones particularly suitable for chain-transferring reactions.

Such were the efforts of Fox and co-workers (*24*) and Gluckman and co-workers (*25*) shown earlier, where mercaptan groups were introduced into the backbone. Ray Chaudhuri and Hermans (*42*) also introduced mercaptan groups into cellulose backbones by reacting ethylene sulfide with cellulose. The same reaction was also carried out on cellulose acetate,

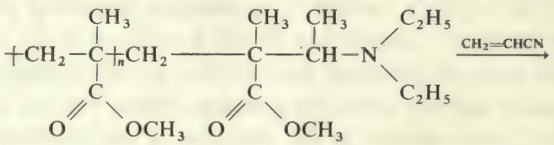


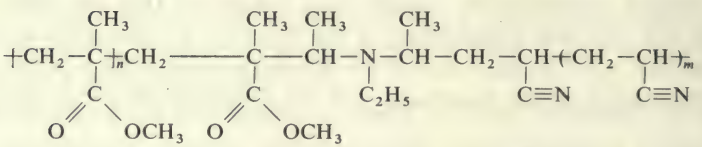
Styrene and methyl methacrylate were then polymerized in the presence of these backbones, yielding graft copolymers.

Schonfeld and Waltcher (*43*) also formed a backbone particularly susceptible to chain transferring by preparing a polyester of adipic acid and pentaerythritol dibromide. The labile halogens acted as the reactive sites,



Bamford and White (*32, 44*) chain-terminated poly(methyl methacrylate) with amine groups. This permitted formation of block copolymers with acrylonitrile, the reaction being initiated by azobisisobutyronitrile,





In a similar manner, block copolymers were formed (*45*) from $-CBr_3$-terminated poly(methyl methacrylate) with polystyrene.

Graft Copolymers from Unsaturated Polymers

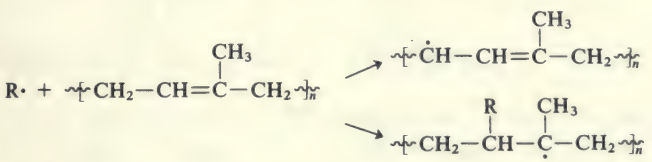
Polymers that possess unsaturated backbones or pendant groups offer reactive sites for radical attack. Grafting reactions to various rubbers, natural and synthetic, have, therefore, been extensively studied (*37, 46–51*). Among

these, methyl methacrylate was grafted to rubber in solution (*45*) using benzoyl peroxide initiator. The reaction product was a mixture of the rubber, methyl methacrylate homopolymer, and the graft copolymer. When the graft copolymer was isolated, it was shown with ozonolysis that the chain lengths of branches approximated those of unattached poly(methyl methacrylate) formed in this reaction. Furthermore, it appeared that approximately one side chain was grafted per each rubber molecule.

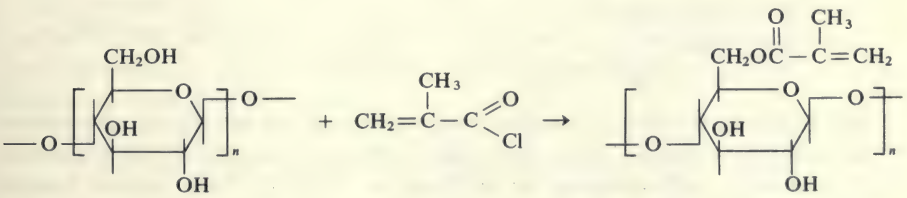
Grafting to natural rubber was also carried out in bulk (*51*) by first swelling the elastomer in methyl methacrylate which contained benzoyl peroxide and then by applying heat. The reaction products were also a mixture of the two homopolymers and of the graft copolymer. In addition, grafting reactions were carried out in emulsion systems on rubber latex. Here it appears that appreciable amounts of grafting took place, although the exact amounts are not generally known. These reactions could be initiated by either water-soluble redox systems or by oil-soluble initiators such as benzoyl peroxide.

Apparently, the efficiency of grafting to rubber is also dependent upon the initiator (*45, 46*). Thus it was demonstrated that use of azobisisobutyronitrile failed to yield graft copolymers, whereas use of benzoyl peroxide gave the desired product.

Allen and co-workers (*46*) used ^{14}C-labeled initiators to study the mechanism of grafting to rubber. The distribution of resultant radioactivity in the polyisoprene backbone before and after ozonolysis demonstrated that free-radical sites are formed in two ways, by addition and by transfer reactions of the primary radical,



Unsaturation can, of course, be deliberately introduced into the backbone to facilitate grafting. For example, to achieve grafting, unsaturation can also be introduced into cellulose, as was done by Berlin and Makarova (*52*), who prereacted it with methacroyl chloride,

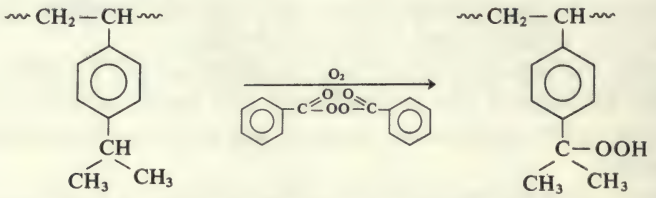


and then were able to graft methyl methacrylate to it.

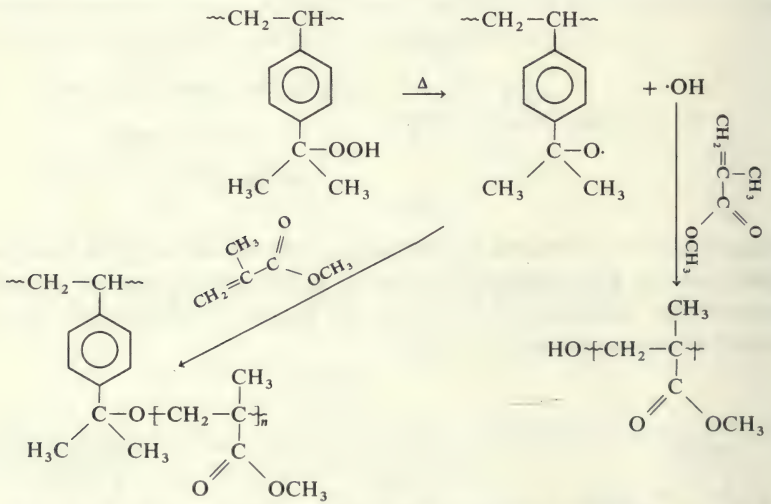
Free-Radical Initiators in Polymer Backbones

Many investigators utilize formation of peroxides and hydroperoxides on the backbone itself to prepare graft copolymers. Once such peroxides are formed, the grafting reaction can be carried out by combining the polymer with the monomer, followed either by application of heat or by addition of redox activators. In such reactions, the amount of attachment will be directly proportional to the number of peroxide groups present.

Hahn and Lechtenbohmer (*53*) attempted to introduce hydroperoxides into polystyrene by oxidation with oxygen. But this approach was apparently not very effective (*54*). It was considerably improved, however, by Metz and Mesrobian (*57*), who oxidized partially isopropylated polystyrene with oxygen in the presence of benzoyl peroxide using isopropyl benzene as the solvent,



Thermal decomposition of the peroxide groups in the presence of methyl methacrylate monomer yielded both a graft copolymer and a homopolymer poly(methyl methacrylate),

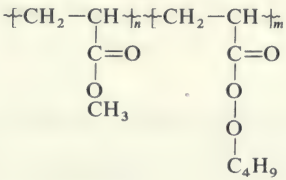


Natta and co-workers (*13*) used a similar technique on atactic polypropylene, which they air-oxidized either in cumene solutions containing some cumene hydroperoxide and methanol or in bulk at 70–80°C. This yielded hydroperoxidized polyolefin, in one case containing as much as 0.8% oxygen. Styrene, methyl methacrylate, and vinyl acetate were then grafted to such

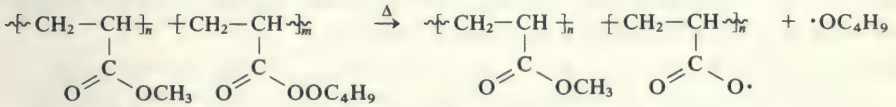
backbones. The same technique applied to solid isotactic polypropylene permitted hydroperoxidation only on the surfaces and in the amorphous regions.

Ozone treatment of the backbone is apparently another means of introducing reactive sites. Thus Korshak and co-workers (*55*, *56*) ozonized polyamides and polyesters and were then able to graft styrene and other vinyl monomers to them. Kargin and co-workers (*57*,*58*) and Plate et al. (*59*,*60*) extended that approach to other backbones, such as starch, amylose, and cellulose, to which they grafted styrene, acrylonitrile, and methyl methacrylate.

Oxidative methods aimed at introducing peroxides into the backbone have the disadvantage of causing oxidative degradations, which accompany many such reactions. Peroxides can, however, be introduced into the backbones via still another technique, as was shown by Smets and co-workers (*61*), who started with a backbone formed by copolymerization of methyl methacrylate with a monomeric perester, in this case *t*-butyl peracrylate,

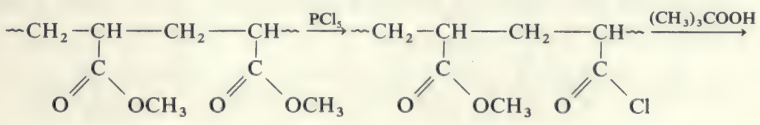


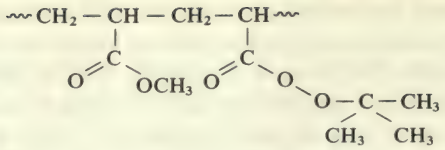
The backbone now was also an initiator for grafting,



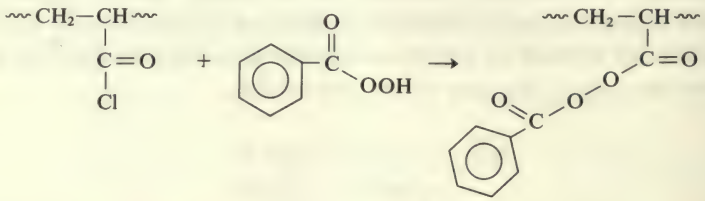
Similarly, block copolymers may also be prepared by first forming peroxide-terminated homopolymers, as was done by Kern and co-workers (*62*) and later by Brepoels and Smets (*63*) when they formed the backbone polymer with the aid of *t*-butyl hydroperoxide in the presence of some cupric ions. This led to the formation of equimolar quantities of butoxy and butyl peroxy radicals, the latter creating chains with terminal peroxy groups in styrene polymerization. When such backbones were used to initiate methyl methacrylate polymerization, poly(styrene-*b*-methyl methacrylate) formed.

Still another method of preparing macromolecular free-radical initiators is to react a poly(acrylate ester), such as poly(methyl acrylate) with PCl_5, and then the resultant acid chloride with a hydroperoxide (*64*), which can then be utilized to form graft copolymers,



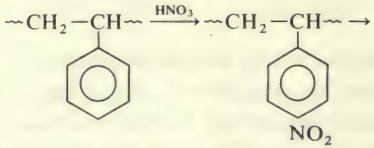


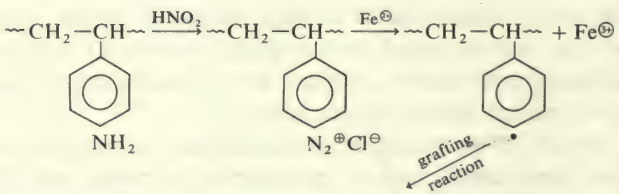
The same results can be obtained through copolymerization of acrylyl chloride with other acrylic esters (*61*, *65*) and then reacting the copolymer with a hydroperoxide. In place of the hydroperoxides one can use peracids, such as perbenzoic, and form polyperanhydrides,



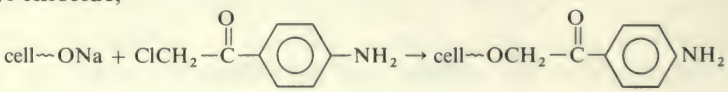
One such reaction was used to form a graft copolymer of methyl methacrylate (*66*) and another one to form a graft copolymer of styrene (*67*).

Valentine and Chapman (*68a*) used a still different approach for the formation of macromolecular initiators by nitrating polystyrene, then reducing the aromatic nitro groups to amine groups followed by diazotization. The diazonium salt was decomposed in the presence of ferrous salts to yield polymeric phenyl radicals capable of initiating vinyl polymerization,

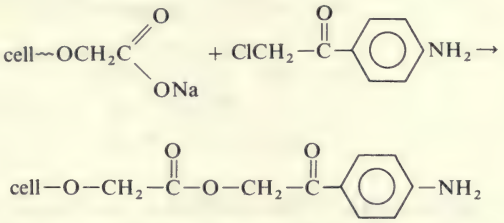




Richards used this method on cellulose (*68b*) by forming diazonium derivatives as initiators for graft copolymerization. The desired aryl amino derivative was first prepared by either (1) reacting mercerized cotton with *p*-aminophenacyl chloride,



or, (2) by reactive sodium carboxymethyl cellulose with this reagent,



The products of these two reactions were then diazotized and grafting polymerizations attempted with styrene, vinyl acetate, and acrylonitrile, using ferrous ions to decompose the diazonium salts. Acrylonitrile grafted readily, but styrene and vinyl acetate apparently did not. Similar results were obtained by earlier investigators in studying grafting reactions to cellulose (*69*) which were carried out by different means.

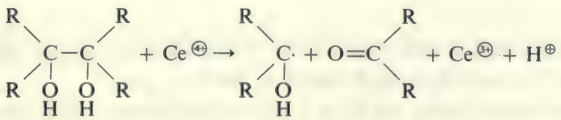
Macromolecular Redox Systems

The principle of this method is based on the ability of ceric ions to oxidize a large number of organic compound, such as alcohols, aldehydes, amines, and thiols (*70*). Transfer of one electron is involved in this oxidation process, causing formation of free radicals,

$$R{-}CH_2OH + Ce^{\oplus 4} \rightarrow R{-}\dot{C}H{-}OH + Ce^{\oplus 3} + H^{\oplus}$$

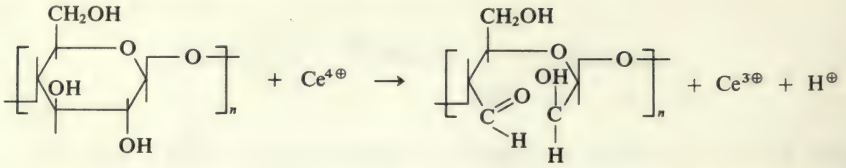
When carried out with poly(vinyl alcohol) (*70*), graft copolymers of acrylonitrile and acrylamide could be formed readily. Almost exclusive formation of radicals in the polymer backbone allows high yields of grafting. This method was also successfully used to prepare cellulose-*g*-polyacrylonitrile (*39*) and starch-*g*-polyacrylonitrile (*71*).

Livshits and co-workers (*72*) attempted to elucidate the mechanism of such grafting reactions to cellulose. They were interested in the site of attack by ceric ions, which they believed to occur on the glycols rather than on primary hydroxyl groups,



The reaction was carried out, therefore, on methyl ethers of cellulose which contained no free glycol groups. Results indicated that no grafting took place. However, when methyl cellulose was used with free glycol groups present, graft copolymerization proceeded at a high rate. This led to the postulate (*72*) of the

following mechanism for radical formation:

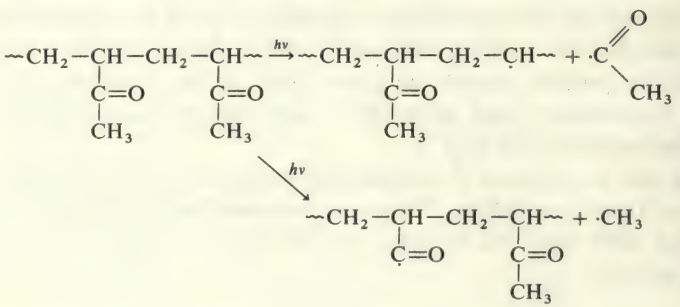


One interesting application of this method of grafting to cellulose with the help of ceric ions was reported by Richards and White (*73*), who grafted acrylonitrile and acrylic acid to paper and formed cation-exchange membranes.

Use of Photosynthetic Methods

If the polymer backbone possesses groups labile to photolysis, then ultraviolet light can be used to form graft or block copolymers. Jones utilized this (*74*) by introducing labile bromine atoms into polystyrene, which he then irradiated in the presence of methyl methacrylate monomer to form poly(styrene-*g*-methyl methacrylate). Significantly, the bromine atoms also caused an accompanying methyl methacrylate homopolymer formation. The average chain lengths of the branches equaled the length of the homopolymer chains.

Ketone groups are also quite susceptible to photolytic decomposition. Guillet and Norrish made use of this fact by forming graft copolymers of acrylonitrile and of methyl methacrylate (*75*, *76*) attached to poly(methyl vinyl ketone) backbones. Poly(vinyl acetate) was also grafted on in the same manner (*76*). The reaction can be shown as follows:

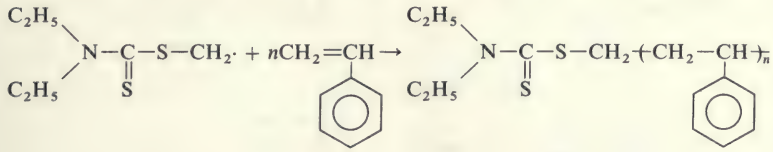


All radicals that form in this reaction are capable of initiating chain growth, with the result that homopolymers formed as well.

Use of photosensitizers, such as 1-chloroanthraquinone, to achieve grafting poly(methyl methacrylate) (*77*, *78*) and polystyrene (*78*) to natural rubber was reported. The reaction was carried out on rubber latices containing monomer and photosensitizer.

Otsu (*79*) has demonstrated that block copolymers can be formed by irradiating with light polymers terminated by special sulfur compounds such as

thiurams. Thus he formed poly(styrene-*b*-methyl methacrylate) by first polymerizing styrene in the presence of a thiuram chain-transfer agent,



The product was then irradiated in the presence of methyl methacrylate monomer with ultraviolet light at 30°C. Approximately 35% block copolymers formed.

The same technique was used to graft poly(methyl methacrylate) to polystyrene when the monomer and polymer were irradiated with ultraviolet light in the presence of the thiuram. Similar techniques also yielded vinyl acetate graft copolymers (*80*).

Actually, direct photoinitiation is only applicable to a few polymer systems. Use of photosensitizers, however, permits broadening this approach considerably. Oster and co-workers (*81, 82*) have explored a number of reactions carried out with the aid of photosensitizers. Grafting of many monomers was achieved to thin films. Thus, for instance, polyacrylamide was grafted to natural rubber with the aid of benzophenone. Others used similar techniques. Poly(vinyl pyrrolidone) was also grafted to dextran by Shen and Eirich (*40*) with the aid of ultraviolet light and benzophenone.

Menon and Kapur studied ultraviolet grafting to rubber latex with the aid of a photosensitizing system based on hydrazine and cupric ions (*83*). The initial reaction is believed to involve formation of hydrazyl radicals,

$$H_2N{-}NH_2 + Cu^{\oplus\oplus} + h\nu \rightarrow H_2N{-}\dot{N}H + Cu^{\oplus} + H^{\oplus}$$

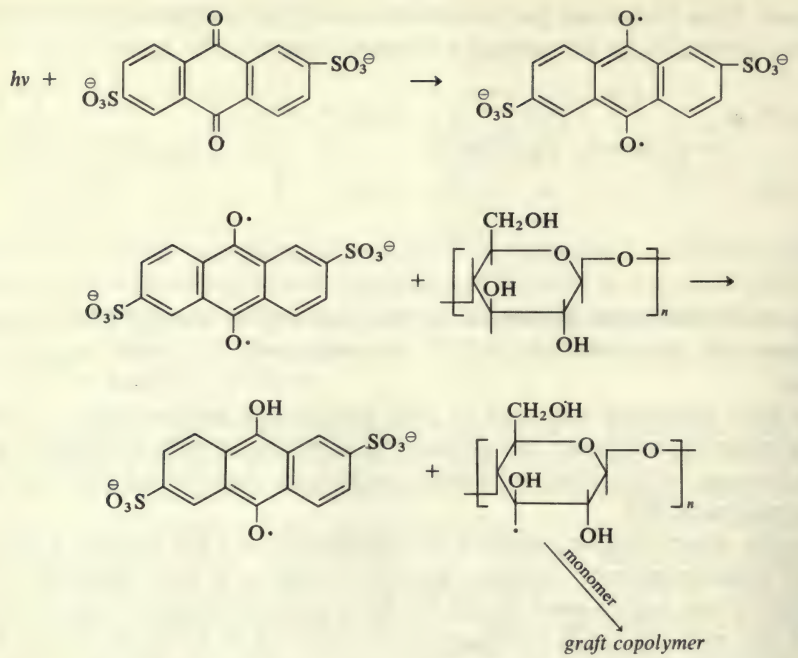
The investigators demonstrated that considerable grafting of poly(methyl methacrylate) can be achieved by this method.

In a similar manner, use can be made of ferric ion pairs in a nitrogen atmosphere to photoinitiate grafting reactions (*83*),

$$Fe^{\oplus\oplus}X^{\ominus} \xrightarrow{h\nu} Fe^{\oplus\oplus}X \rightarrow Fe^{\oplus\oplus} + X\cdot$$

$$X\cdot + \text{monomer} \longrightarrow X\,\text{monomer}\cdot, \text{ etc.}$$

Use of phototendering dyes is still another technique that has been utilized for grafting. Stannett and co-workers (*91*), and Chapiro (*92, 93*) grafted monomers to cellulose in the presence of anthraquinone dyes. The dyes adsorb to cellulose and upon irradiation abstract a proton from the substrate, thereby creating free radicals on the backbone,



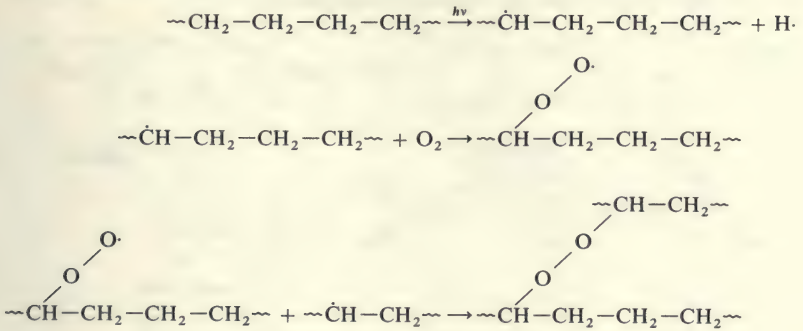
The dye monoradicals (above) are believed to disproportionate to hydroquinones and quinones. Transfer reactions with solvent and monomer cause formations of homopolymers. Use of this method enabled preparation of graft copolymers of poly(methyl methacrylate) and polyacrylonitrile to cellulose (*84*). Only small amounts of grafting, however, were possible with styrene and vinyl acetate (*69*).

Use of High-Energy Radiation

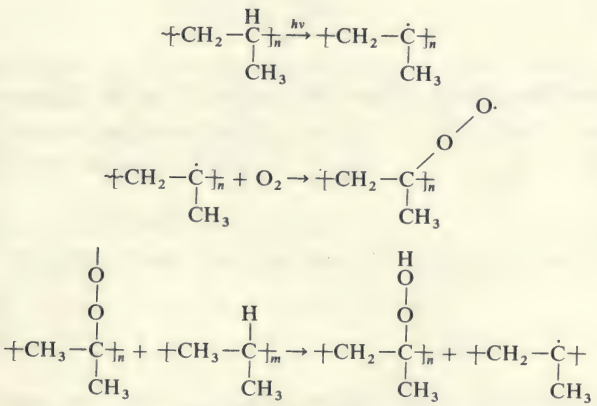
High-energy radiation includes use of gamma rays from radioactive sources, such as cobalt-60; electron beams, such as a Van de Graaff generator; and nuclear reactors. Radiation of 100 eV or greater is particularly effective in rupturing chemical bonds and creating free radicals that can be utilized for the grafting reaction. Irradiation of the polymer backbones in open air or in an oxygen atmosphere is a means for producing hydroperoxides and peroxides on these backbones. Such material can later be used in the grafting reaction. The polymer can also be irradiated in vacuo to form trapped radicals. Subsequently, this polymer can be swollen by a monomer in an inert atmosphere to accomplish grafting. Third, one can preswell a polymer with a monomer and then irradiate the two together to accomplish grafting.

The first method was studied by Chapiro (*85–87*). He postulated that irradiation of polyethylene leads to peroxide formations, whereas that of polypropylene leads to hydroperoxide formation:

Polyethylene:



Polypropylene:



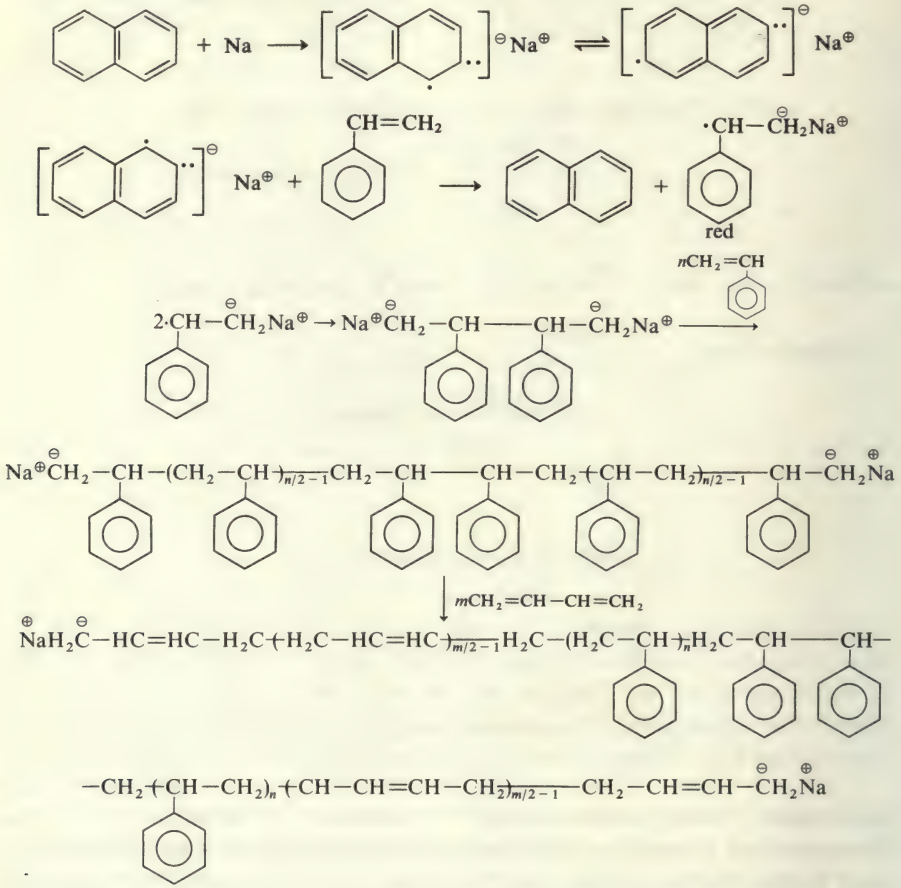
Significantly, when polymerization of monomers is initiated by thermal decomposition of such peroxides and hydroperoxides, the latter cause much more homopolymer to form than the former. This is because hydroperoxides give rise to unattached hydroxyl radicals (*87*). Formation of homopolymer can be reduced by carrying the reaction out at room temperature with the aid of a redox system (*88*).

When one is carrying out irradiation of polymers swollen by some monomer, efficient grafting depends largely upon the ability of forming most of the free radicals on the polymer backbone. Otherwise, homopolymers will largely result.

Ionic Syntheses of Graft on Block Copolymers

The most prominent method for forming block copolymers by ionic means is with the aid of "living" polymers (Chapter 5). The "living" ends of a desired polymer may initiate polymerization of another monomer, thereby leading to block copolymers free of any homopolymers. Actually, copolymers containing

more than two or three blocks per molecule were prepared by this method (*89–91*). The method can be readily illustrated as follows:



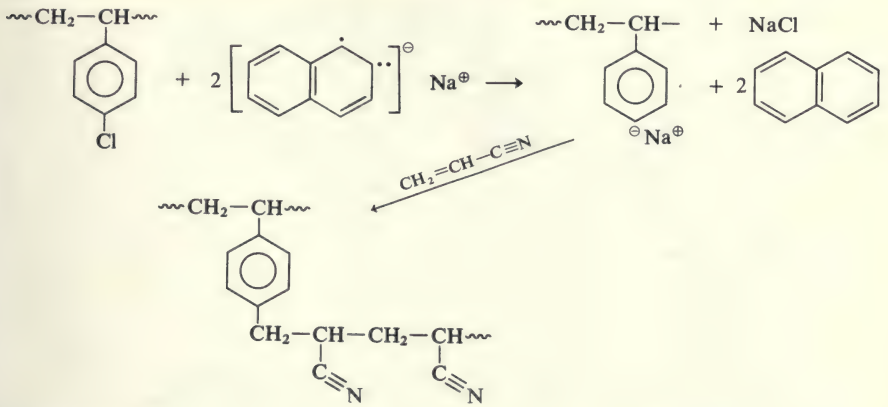
Some drawbacks to this method were reported. Thus when methyl methacrylate is used initially, block copolymerization with styrene will apparently not proceed.

O'Driscoll and co-workers (*6*) observed that in "living" polymers formed by lithium-initiated copolymerization of styrene and methyl methacrylate, only the anionic end added methyl methacrylate, whereas the free-radical end caused random copolymerization of both monomers.

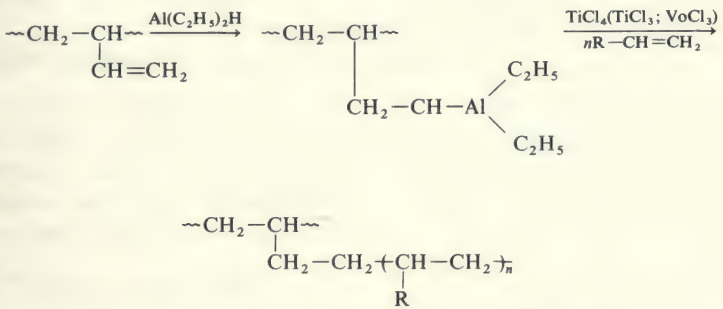
Epoxide monomers can also add to the "living" carbanions. Thus Richards and Szwarc (*92*) formed poly(styrene-*b*-ethylene oxide), poly(styrene-*b*-propylene oxide), and poly(styrene-*b*-styrene oxide) block copolymers.

Greber and Tolle reported (*93*) that graft copolymers may be formed on polychlorostyrene by such anionic mechanism. When poly(*p*-chlorostyrene) was reacted with sodium naphthalene, the product initiated graft formations of

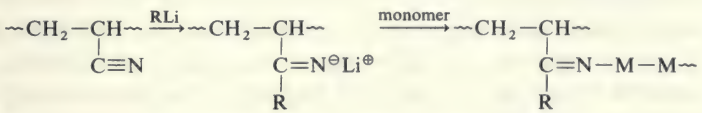
polyacrylonitrile, poly(vinyl pyridine), poly(methyl methacrylate), and polystyrene,



Also, Ziegler-type catalysts were formed from a 1,2-butadiene adduct in a copolymer of butadiene and styrene (*94*). The vinyl double bond was first reacted with diethylaluminum hydride and then with a transition-metal halide to yield active catalysts for α-olefins,

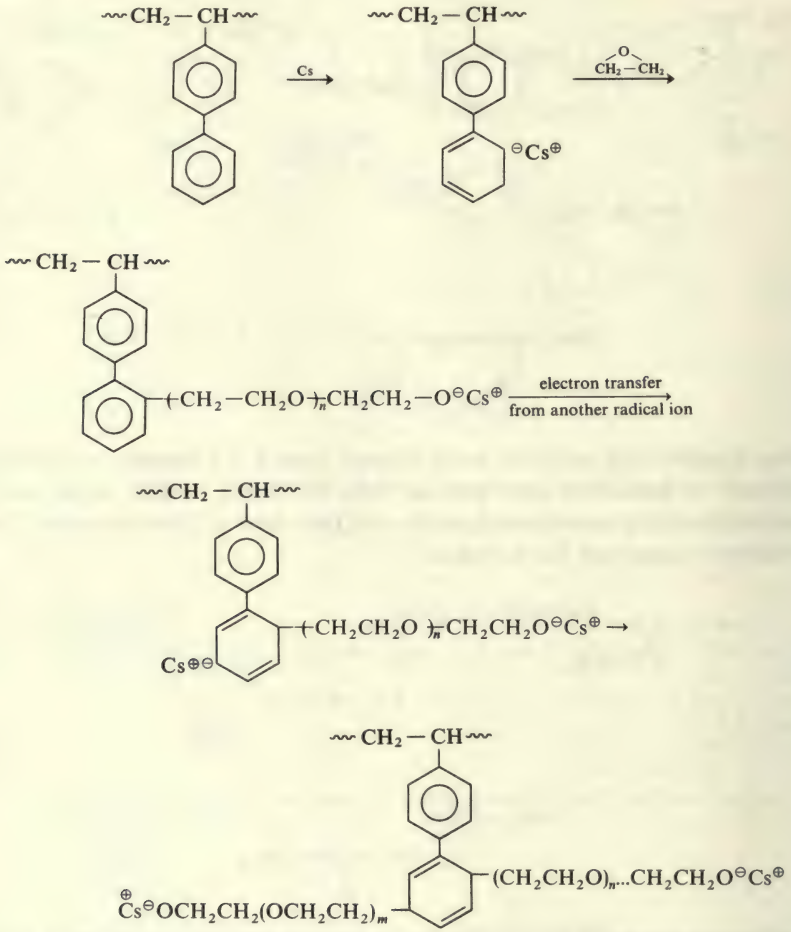


It was also shown (*94*) that the nitrile groups present in polymers and copolymers of acrylonitrile (and other nitrile-group-bearing polymers) can be utilized for grafting reactions by prereacting them first with alkyllithium or Grignard reagent,



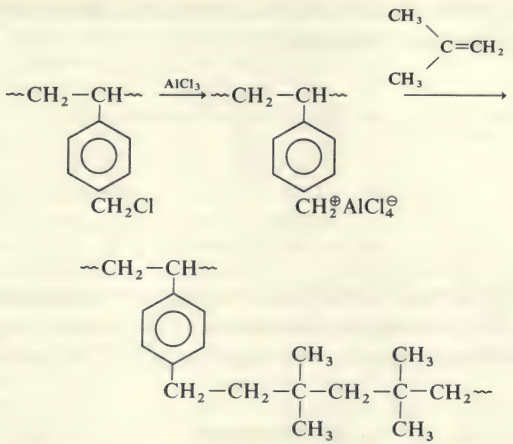
Another interesting reaction was carried out on polymers with pendant aromatic groups. Polyradicals anions were formed first with alkali metals in tetrahydrofuran (*95,96*). The resultant radical anions then initiated polymerizations of vinyl monomers by the electron-transfer process. When ethylene

oxide was introduced, graft copolymers formed via bond formation to the initiator,



Feit and co-workers (*97*) carried out anionic grafting of vinyl monomers to cellulose and poly(vinyl alcohol). Here alkali alkoxides of these backbone polymers were used as initiators, with graft polymerizations carried out in liquid ammonia or other solvents at low temperatures. The vinyl monomers used in these studies were acrylonitrile, methacrylonitrile, and methyl methacrylate. Chain transferring in liquid ammonia caused considerable homopolymerizations in addition to the graft formation. No cross-linking was observed during the reactions.

Halogen-bearing polymers such as chlorinated polystyrene, poly(vinyl chloride), and poly(vinylidine chloride) copolymers can also be used to carry out graft copolymer formations by cationic mechanism. Such materials will react (*98,99*) with $AlCl_3$ to form typical cationic initiators,

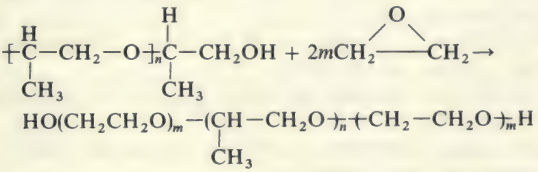


Side reactions in these syntheses cause cross-linking and decomposition.

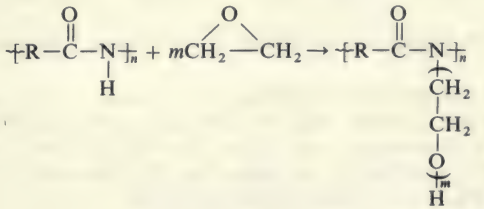
Jaacks and Kern (*100*) reported graft and block copolymer formation on polymers bearing C—O—C groups, such as poly(vinyl acetate), polyesters, and polyethers which act as chain-transferring agents in cationic polymerization of trioxane. The structure of the backbone polymer determines whether graft copolymers, or block copolymers form, or whether cross-linking takes place.

Saturated Backbones with Acidic or Basic Groups

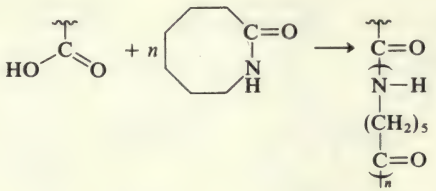
Block copolymers of ethylene and propylene oxides fall into this category. The copolymers are formed quite readily, because terminal hydroxyl groups on these polymers can be utilized for initiation of copolymerization (*101*). Thus polypropylene oxide can be used to initiate ethylene oxide polymerization to form block copolymers, and vice versa,



Hydrogens on polyamide backbones are acidic enough to initiate ethylene oxide polymerization to form graft copolymers (*102*),



Or one can graft coprolactam polymers to pendant acidic group (*103*) resulting in polymers with polyamide branches,



Finally, hydroxyl atoms of cellulose can initiate ring-opening polymerizations of lactones (*103,104*) and of ethyleneimine (*105*) as well as polymerizations of epoxy (*106*) and of melamime- and urea-formaldehyde resins (*107*).

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Reactions of Polymers

24

24-1. Reactivity of Functional Groups in Polymers

Some organic reactions of high polymers appear to proceed at slower rates; others appear to proceed at faster rates than comparable reactions of corresponding small molecules. An example of this would be catalytic hydrogenations of macromolecules possessing double bonds. Such reactions usually proceed at much slower rates than those of simple, low-molecular-weight olefins. An example of the opposite situation would be typical enzymatic reactions which exhibit very high rates at low concentrations. Somewhat similar phenomenon was observed by Morawetz et al. (*1*,*2*) in some synthetic polymers. Copolymers of *p*-nitrophenyl methacrylate with acrylic acid tended to hydrolyze much more rapidly than *p*-nitrophenyl esters of monocarboxylic acids.

However, in many cases involving reactions of functional groups in polymers, we can expect the rates to be the same, or essentially the same as those exhibited by their low-molecular-weight homologs. Alfrey (*3*) postulated conditions when this will be true!

1. In reactions taking place under homogeneous conditions in a liquid medium with all components, reactants, intermediates, and products being soluble in the reaction medium.

2. Only one polymer-attached functional group participates in each elementary step of the reaction, the remaining species being small and mobile.

3. The low-molecular-weight "homolog" is chosen with sufficient care, so that all steric factors occurring in the immediate vicinity of the chain are taken into proper consideration.

On the opposite side of this would be a list of conditions in which polymers would exhibit unequal reactivities to their low-molecular-weight homologs. These would actually be exceptions to Flory's basic postulate (*4*) that polymers exhibit the same reactivity of functional groups as do small molecules. Morawetz (*5*) divides these conditions into four categories:

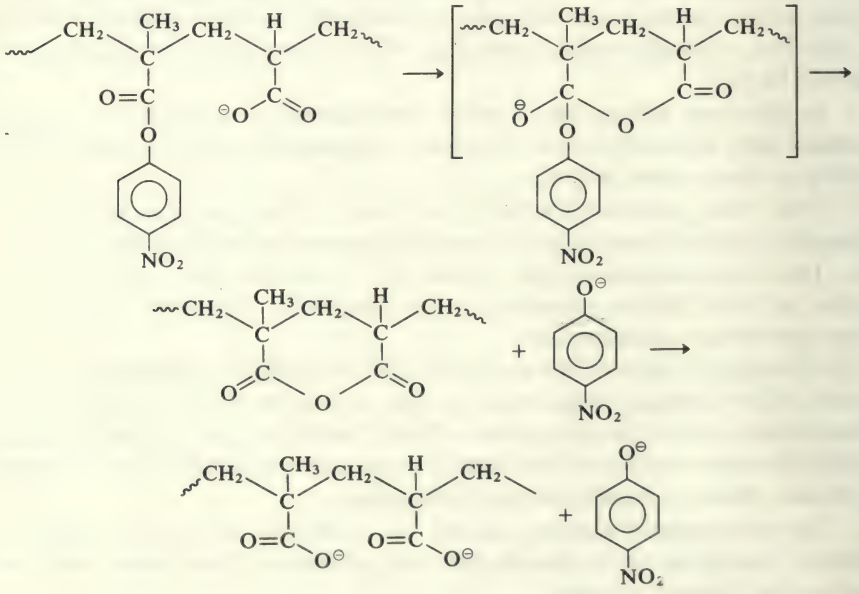
1. The electrostatic charges carried by polymers can extend over considerable distances. Such charges can exert profound effects upon reactions that involve charged reagents.

2. When the interaction of two neighboring functional groups on a polymer leads to a five- or six-membered cyclic transition state, then a neighboring group effect may modify reactivity of these functional groups. This can be expected to be qualitatively similar to effects in a bifunctional analog.

3. Chain flexibility may cause interaction of functional groups spaced further apart along the polymer chain to become important. This may be enhanced by the large number of functional groups present, which may be constrained to occupy the limited volumes of swollen polymer chains. So, reactivity of dilute solutions of polymers may approximate that to be expected of a system composed of droplets of concentrated solution separated by long distances of pure solvent.

4. Specific chain folding may force functional groups into mutual proximity, causing interreactions. This would not occur were the polymer randomly coiled, thereby creating little chance for interaction of such groups placed along the polymer backbone. An example of such chain folding would be in a globular protein.

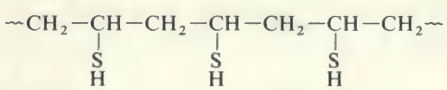
Among the effects listed, perhaps the most noteworthy one to an organic chemist would be the neighboring group effect. Such an effect was observed by Morawetz and co-workers (*1,2*) with *p*-nitrophenyl esters on large and small molecules. The rates of hydrolysis of such esters were studied under conditions which would normally be controlled by hydroxyl ion catalysis. The observed high reactivity of ester groups of polyanions was the opposite of what was expected. The apparent reason for this was the fact that the hydrolysis was actually caused by attacks of neighboring ionized carboxyl groups on carbonyl carbons of the ester groups,



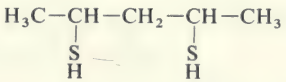
Any such neighboring group effect will depend, of course, on the distance or spacing of the two groups from each other. Thus it was shown (*6*) that succinic acid monoesters are many times more reactive than glutaric acid monoesters. Steric location of functional groups on the polymer backbone with respect to each other should also influence neighboring group effects. Thus, in copolymers of methacrylic acid and *p*-nitrophenyl methacrylate, Morawetz and Gaetjens (*7,8*) found that hydrolysis deviated from first-order kinetics. In fact, they concluded that the copolymer behaved as if it possessed two different kinds of ester groups, with approximately 20% of them being about 10 times as reactive as the rest. This was explained on the basis of steric relationship of the groups, where the asymmetric carbons carrying the ester and the catalyzing carboxylate groups, respectively, have either the same or opposite steric configurations.

Overberger and Bousignore (*9*) observed that the oxidation rate of mercaptans attached to macromolecular backbones differs significantly from the oxidation rate for simple molecules. Poly(*p*-vinyl phenyl thiol) was oxidized in an aqueous solution at pH 10, almost eight times as rapidly as *p*-thiocresol, but only 20% faster than 2,4-di(*p*-mercaptophenyl) pentane.

In a similar study, Overberger and Ferraro (*10*) compared oxidation rates of hydrolyzed poly(vinyl thioacetate),



with that of 2,4-dimercaptopentane,



Here, too, the macromolecule was found to be 10 times as reactive as its bifunctional analog. This shows, of course, that interaction of pairs of thiol groups, other than those of nearest neighbours, contribute to the rate.

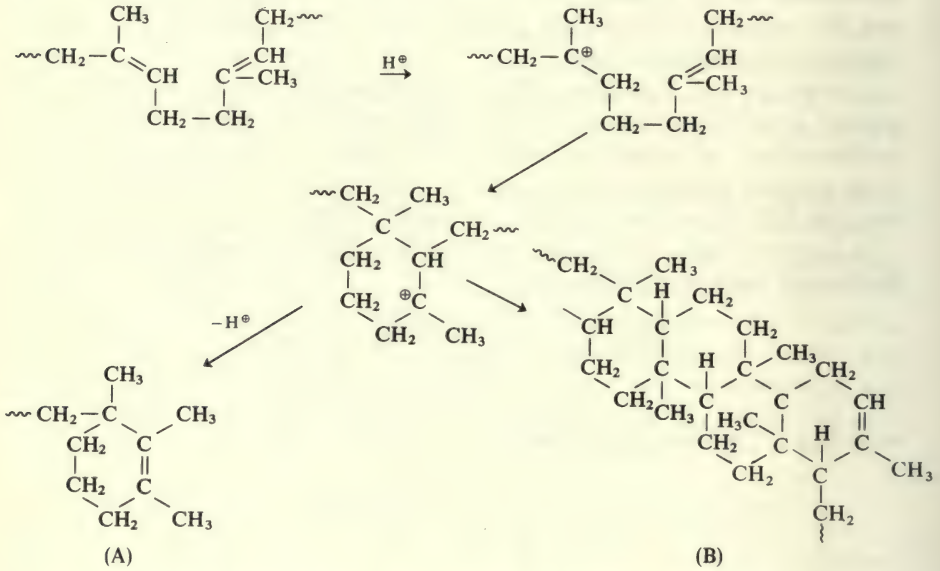
Morphological differences in polymers also exhibit strong influences on reactivities of macromolecules. This is the result of differences that arise in accessibility of various functional groups to the reaction site and may be considered a manifestation of steric hindrance.

A special situation arises when the electrical potential of the polymer molecule increases during the course of reaction and the charged groups are simultaneously carried by the backbone into direct vicinity of the reacting groups. Such a phenomenon was demonstrated by Katchalsky and co-workers (*11,12*) who first calculated the electrostatic potential of a macromolecule carrying a given number of charges distributed statistically along the chain. This was done as a function of the degree of ionization and ionic strength of the solution, taking in consideration the end-to-end distances of the uncharged molecules,

as well as that of the stretched ionized molecules. The validity of this calculation was then tested on a case of alkaline hydrolysis of pectinic acid (*12*). As the reaction proceeded, a typical decrease in rate was observed. This rate, however, increased when the ionic strength of the solution increased.

24-2. Isomerization of Polymers

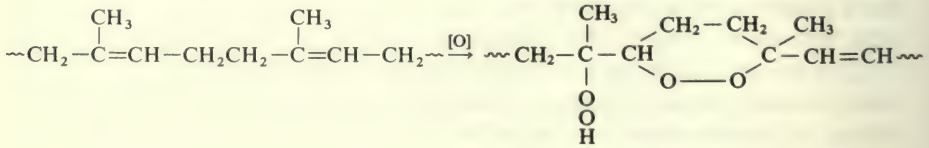
A typical case of isomerization in polymers is the cyclization reaction common to natural rubbers and polymers from dienes (*13*) (such as synthetic polyisoprene), which can be caused by Lewis acid or H_2SO_4,



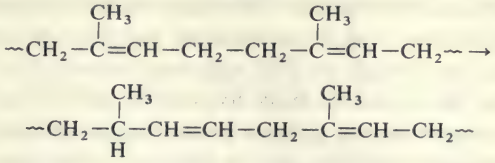
The reaction is believed to proceed via carbonium ion mechanism. The structure of the end product has as yet, however, not been fully settled. It may be monocyclic (A) (*14–16*) or polycyclic (B) (*17–19*). Golub and Heller (*20,21*) presented evidence, however, in favor of structure (B). The product of this reaction is no longer an elastomer, but a hard material, having lost much of its original unsaturation.

Shifts of double bonds are common to many macroolefins and occur in the course of chemical reactions. Thus oxidation of hevea rubber was found to be accompanied by a double-bond shift (*22–24*).

(A) Regular oxidation path:



(B) At temperatures of 150°C and higher, a shift occurs (*25*):

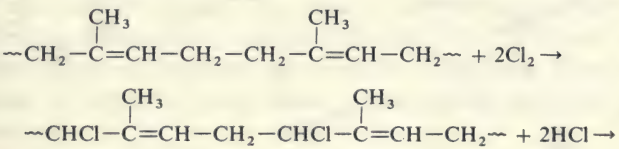


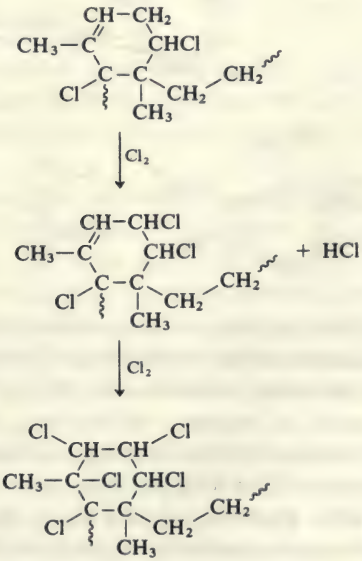
24-3. Halogenation of Unsaturated Macromolecules

An interesting reaction of polymers is halogenation of rubbers. Several reactions appear to take place at the same time and the mechanism is still not fully elucidated.

It is believed that in chlorination of natural rubber (*26–30*) four different reactions can take place: (1) substitutive chlorination, (2) addition to the double bond, (3) cyclization, and (4) cross-linking. The course of the reaction appears to be somewhat dependent on the halogenating agent and solvent used.

When halogenation is conducted with chlorine in carbon tetrachloride the reaction can be described as follows:



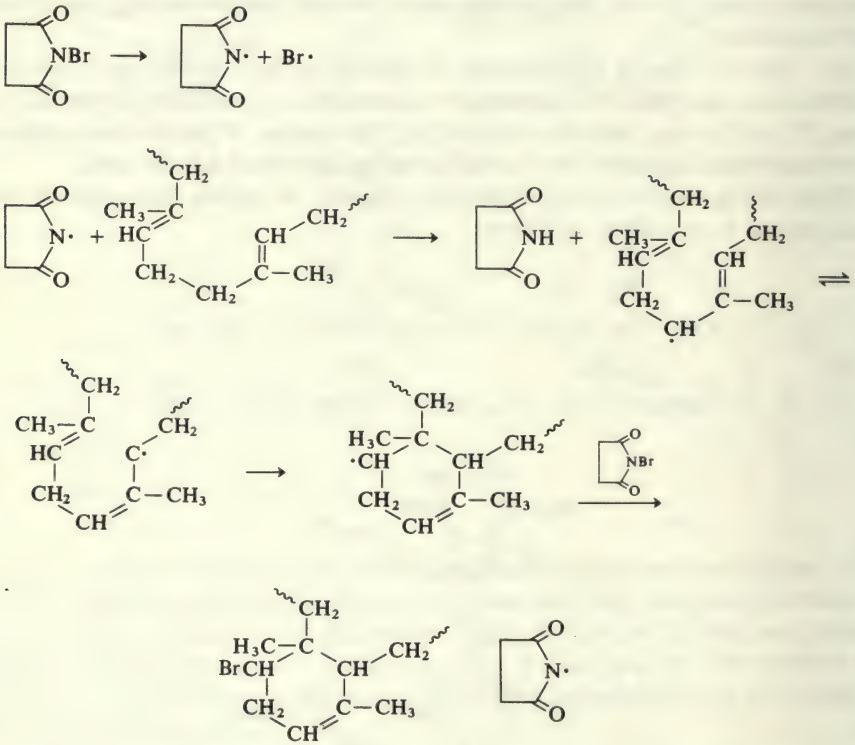


It is not established yet whether the substitution reaction takes place by a free radical or by an ionic mechanism. This is also true of the cyclization reaction.

When chlorination is carried out in benzene, the reaction appears to proceed without cyclization to as high as 30% chlorine content (*31*). Bromination of rubber, on the other hand, can be made to proceed entirely additively if carried out at 0°C with trace amounts of alcohol present in the solvent (*27*).

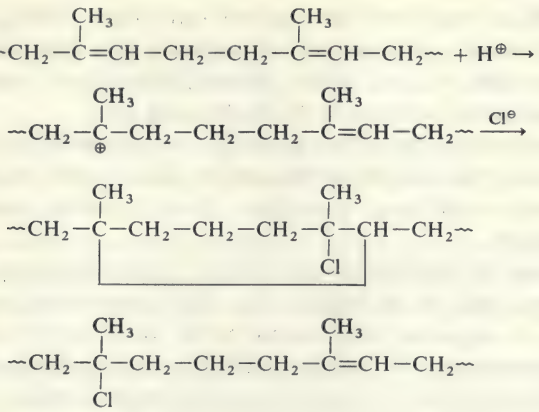
Additive chlorination reactions can be achieved when phenyl iodochloride or sulfuryl chloride are used as the chlorinating agents with traces of peroxides present in the reaction medium (*28*).

N-bromosuccinimide was shown (*28*) to give substitutive halogenations accompanying cyclization with natural rubber:



The behavior of synthetic rubbers in halogenation is different. Thus polymers and copolymers of butadiene tend to precipitate during chlorination when a reaction is carried out in carbon tetrachloride (*26,32*). This can be avoided by using other solvents, such as benzene, chloroform, ethylene dichloride, and mixed solvent (*32,33*). Generally, cross-linking reactions are much more pronounced with polybutadiene than with polyisoprene.

Polyisoprenes will also hydrohalogenate quite readily in solution. The reaction was shown to be accompanied by cyclization (*26*),



or

24-4. Epoxidation of Macromolecules

Epoxidation reactions of olefins lead to oxirane structures and/or glycols depending on reaction conditions. This is well known in organic chemistry and was the subject of a review article (*34*). When the reaction is carried out with macroolefins, use of organic peroxides as in the Prileschaeff reaction appears to yield most satisfactory results. The reaction is best carried out in solution, although use of an emulsion system was reported (*35*). The products of epoxidation are typical epirane ring-bearing materials. If the epoxidized polymer is a polybutadiene or a polyisoprene, then products with multiple oxirane rings can be prepared.

24-5. Substitution Reactions

Many substitution reactions have been carried out on polyolefins. Some of these reactions are hydride transfers catalyzed by Lewis acids (*36*). Most processes of aliphatic substitution, however, probably proceed by free-radical mechanism.

Among the more important substitution reactions of polymers should be listed halogenations of polyolefins. Fluorination of polyethylene is possible in the dark. When film or powder are exposed to fluorine vapor diluted with up to 10% nitrogen, the halogen must be introduced slowly to prevent destruction of the polymer (*37,38*). The reaction apparently only occurs on the surface. It was reported, however, that complete fluorination is possible with reactions conducted over several days with 3-mil film on a 100-mesh phosphor bronze gauze (*39*).

Use of mercuric or cupric fluoride in hydrofluoric acid was reported to result in addition of 20% fluorine to polyethylene in 50 hours at 110°C (*40*).

Polyethylene can be chlorinated in the dark at 150°C without the aid of an initiator. It is quite likely that residual peroxides might be acting here as

initiators. When reactions are carried out below 100°C, oxygen must be removed to prevent inhibition and degradation (*41*). Cross-linking is promoted by ultraviolet light beyond 2500 A. When chlorination is conducted in boiling carbon tetrachloride, azo catalysts can be used (*42*).

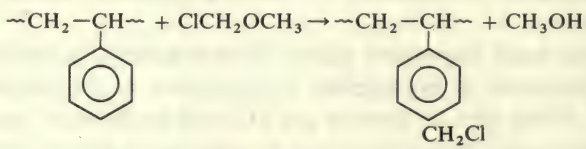
Chlorination of polypropylene is usually accompanied by severe degradation. It was reported that polypropylene can be chlorinated in the dark by mixing its fine powder with large quantities of salt, thereby causing perhaps less degradation (*43*).

Chlorination of poly(vinyl chloride) is a commercially used process for preparing materials with higher T_g's. The process (*44*) consists of photochlorination in aqueous suspension in the presence of chloroform at mild temperatures (approx. 55°C). When sufficient chlorine is introduced, it is possible to form 90 mole % of 1,2-dichloride groups and 2.6 mole % of 1,1-dichloride groups. Dry photochlorination of poly(vinylchloride) was also reported to be possible (*45*).

Other reactions of polyolefins, such as chlorosulfonation, are known. Pyridine in less than stoichiometric amounts may be added (*46*) as a catalyst. The base is believed to complex with sulfuryl chloride and HCl thereby favoring chlorosulfonation.

24-6. Nuclear Substitutions of Poly(vinyl aromatics)

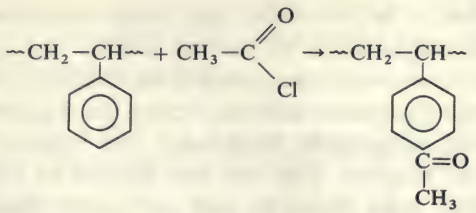
A number of reactions are possible with polystyrene and its analogs, such as vinyl toluene. Thus polystyrene can be chloromethylated and chlorosulfonated to yield ion-exchange resins (*47*). Chloromethylation proceeds readily with chloromethyl ether in the presence of Lewis acids. The product of this reaction is methanol, which tends to slow it down with increased conversion. Cross-linking will also accompany the reaction, so a large excess of chloromethyl ether is favored together with the use of low-molecular-weight polystyrene. Zinc chloride (or zinc oxide) is the favorite Friedel-Crafts catalyst:



The reaction can also be carried out with formaldehyde and methanol, using aluminum chloride as the catalyst in ethylene dichloride solvent or swelling agent (*48*).

Alkylation of polystyrene with methyl undecylenate at 85°C using aluminum chloride catalyst was reported (*49*). The reaction was carried to 50% conversion.

Acylation of styrene with acetyl chloride in carbon disulfide or in carbon tetrachloride was also reported. The reaction was found to result in high conversions (*50,51*),

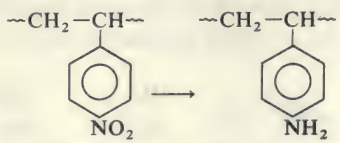


Sulfonation reactions of poly(vinyl aromatics) are usually accompanied by cross-linking. There is some evidence that the cross-links are sulfonic anhydrides, which are hydrolyzable. This was observed by Roth, who carried out the reaction with sulfur trioxide (*52,53*).

Partial sulfonation yields water-soluble products at above 50% conversion and aqueous-organic solvents soluble products above 25% sulfonation (*54,55*).

Polystyrene was first nitrated in 1845 with fuming nitric acid (*56*). This yielded a product containing 11% nitrogen (*57*). A dinitro derivative of polystyrene can be prepared with the aid of nitric acid–sulfuric acid mixtures capable of dissolving the polymer (*58,59*). The dinitro derivative is only swellable in acetone but soluble in dimethyl formamide.

The nitrated polystyrene can be reduced to the corresponding amino derivative (as mentioned in Chapter 23),



Bachman obtained good results with ammoniacal sodium hydrosulfite as the reducing agent (*57*). Catalytic reduction is also possible (*60*).

Styrene–divinyl benzene copolymer was reported as having been nitrated, reduced, diazotized, and treated with potassium xanthogenate to form a cross-linked mercaptostyrene (*61*).

Nuclear halogenation of poly(vinyl aromatics) takes place readily in the dark. Polystyrene was also reported to have been chlorinated with liquid chlorine solution at atmospheric pressure. A variety of solvents could be employed (*62*).

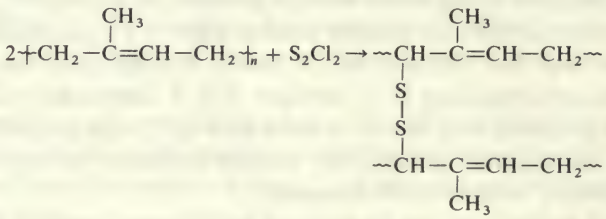
Often side-chain halogenation accompanies the reactions with a tendency to cross-link in spite of an opposite tendency to cause degradation by the Friedel-Crafts catalysts (*63*).

24-7. Cross-Linking of Elastomers

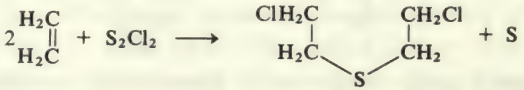
Cross-linking (vulcanization) of rubber is a very important industrial process which has attracted attention of scientists for a long time. Back in 1894, Weber explained (*64*) the vulcanization of rubber with S_2Cl_2 as follows:

$$C_{10}H_{16} + S_2Cl_2 \rightarrow C_{10}H_{16}S_2Cl_2$$

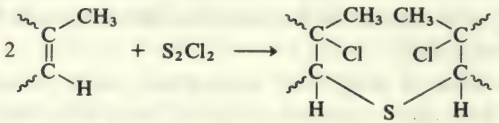
The above was based on Weber's belief that rubber molecules are multiples of $C_{10}H_{16}$ (rather than polyisoprene, as we now know). The term *vulcanization* is the rubber industry's synonym for cross-linking at certain conditions or to a certain degree. The most common method of cross-linking rubber is with sulfur or with sulfur-bearing compounds. Studebaker and Nabors (*65*) investigated the mechanism of this reaction. This was also studied by Moore (*66*) and by Bevilacqua (*67*). Their work indicates that such sulfur-bearing compounds as tetramethylthiuram disulfide or others insert mainly monosulfide cross-links into rubber. On the other hand, Glazer and Cotton (*68*) reported that the cross-link which forms in natural rubber, when heat-cured with sulfur monochloride, is a disulfide,



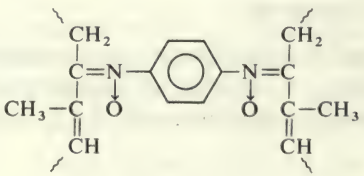
This appears to be different from reactions carried out in the cold. When rubber is reacted with sulfur chloride in the cold, one atom of sulfur is liberated (*68*) and appears as amorphous sulfur, similar to the formation of mustard gas,



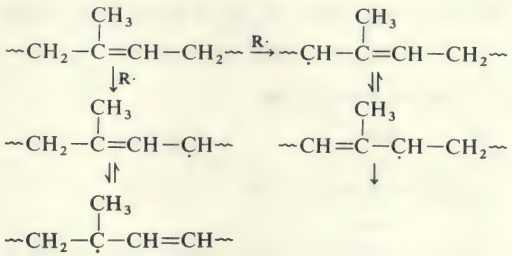
So, by analogy, the vulcanization in the cold would result in monosulfide links,



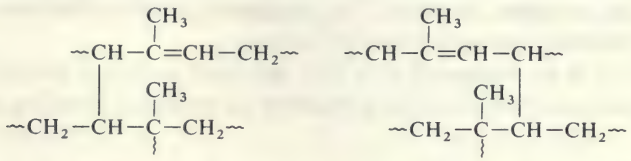
Sulfur, of course, it not the only material that will cross-link rubber. It is interesting that 1,3,5-trinitrobenzene and *meta*- and *para*-dinitrosobenzene will also vulcanize rubber in a manner similar to sulfur. In addition, nitrose groups were shown (*69*) to react with rubber chains, leaving the double bonds intact but forming cross-links,



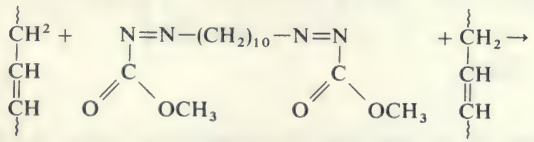
Use of peroxides for cross-linking rubbers is also well known. The reaction is probably that of the double bonds of the neighboring chains. Attacks on the allylic carbon must occur as well,

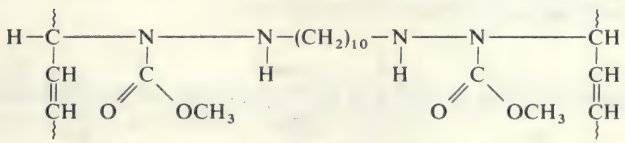


with the result that some cross-links can be pictured as follows:



In addition, it is possible to vulcanize rubber with bisazotetracarboxiylic esters (*70*). The reaction take place in the following manner:

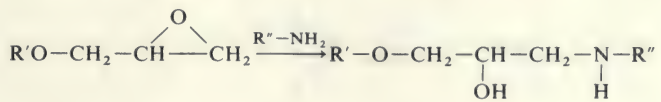




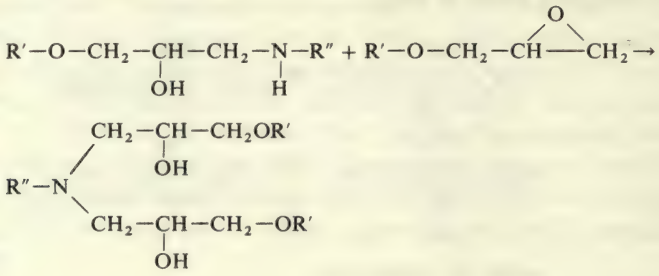
24-8. Cross-Linking of Epoxy Resins

The mechanism of cure of epoxy resins is quite challenging, because a number of simultaneous reactions appear to be taking place. The rate of cross-linking has been studied by a number of methods. One such technique is to measure rate of disappearance of some specific infrared absorption bands in the spectra (*71*).

When primary or secondary amines are used to cross-link epoxy resins, the main reaction is as follows (*71–75*):

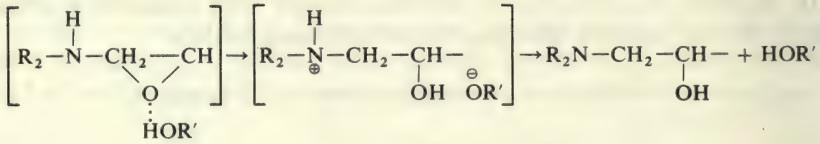


Secondary amine groups will react as rapidly with epoxide groups as the primary ones, barring steric hindrance,

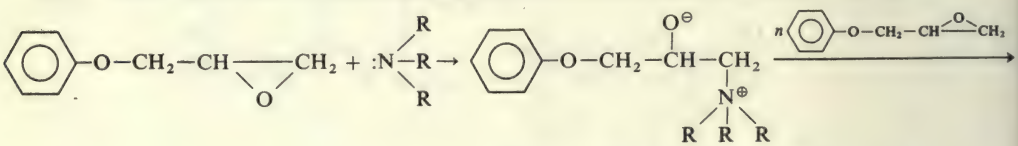


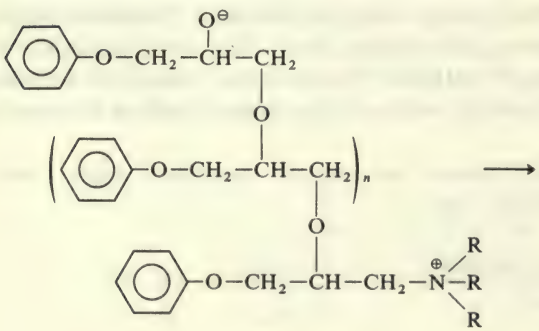
Tertiary amines will also catalyze epoxy polymerizations. The product from the above reaction, however, has apparently little effect on epoxy groups (*76,77*), probably because of steric hindrance.

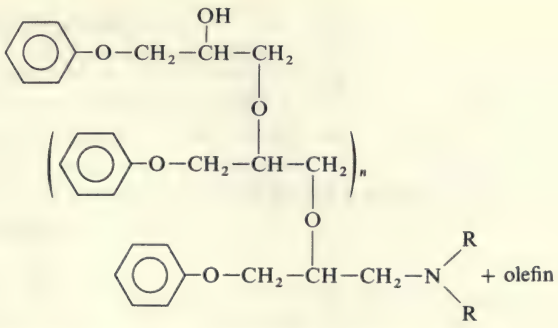
Shechter et al. suggested (*73*) that one part hydroxyl groups participate in epoxy reactions by assisting ring opening via hydrogen bonding in the transition state,



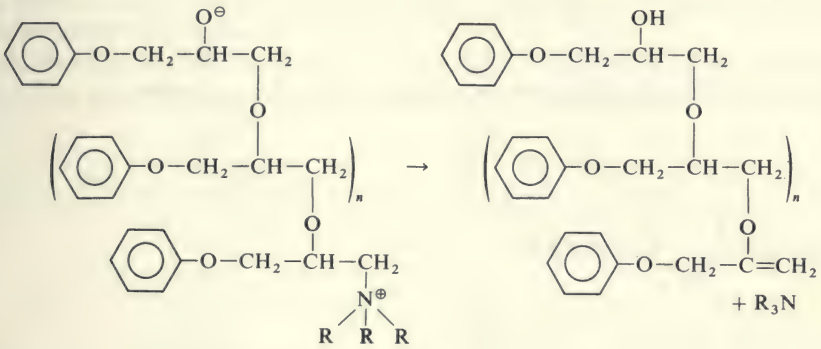
The reaction of the tertiary amines in catalyzing epoxy polymerization can be shown on phenylglycidyl ether (*72*) as follows:



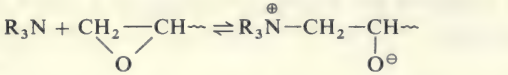


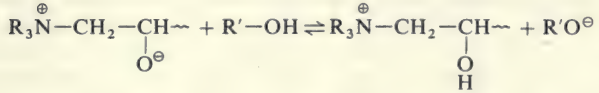


Narracott (*72*) observed that when triethyl amine was used, ethylene and traces of nitrogen were found in the product. Polymer fractions with residual unsaturation were also observed. This suggests that some termination resulted as follows:

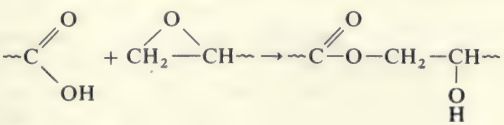


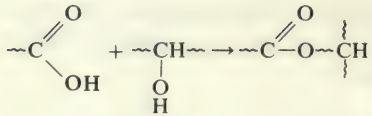
Here the tertiary amine acts as a true catalyst. Tertiary amines are also known to catalyze reactions of epoxies with hydroxyl groups (*71*),

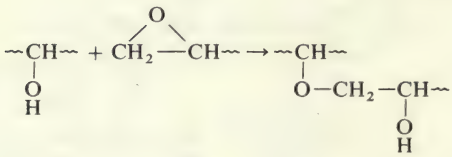


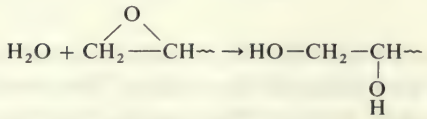


When carboxylic acids are used to cause cross-linking of epoxy resins, four reactions can be expected (*76*),

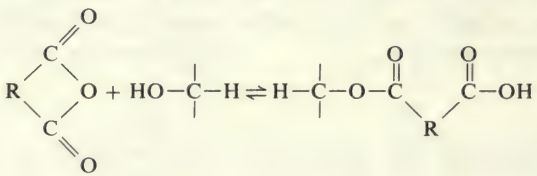


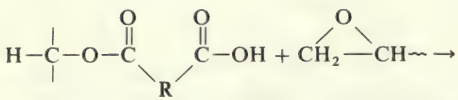


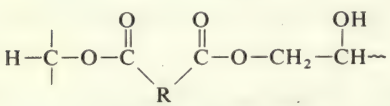




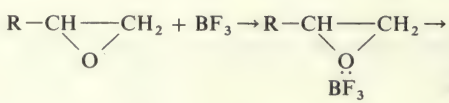
Acid anhydrides are also capable of opening epirane rings (*78–82*),

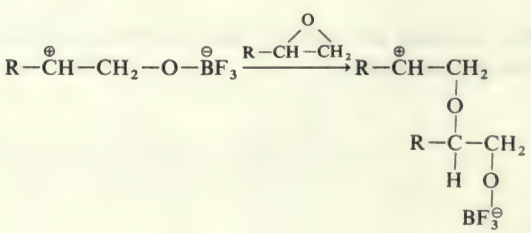






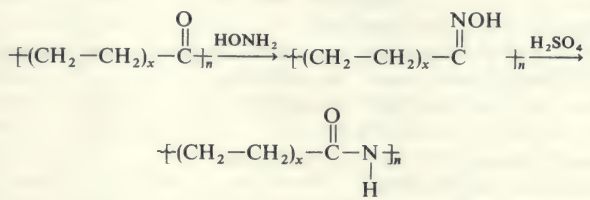
Finally, Lewis acids are also capable of catalyzing reactions of epoxy resins. Particularly effective are boron trifluoride and metal halide complexes with polyethers (*83,84*),





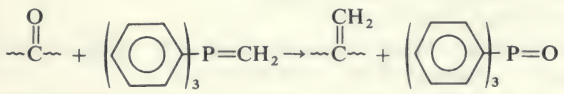
24-8. Miscellaneous Reactions

A number of reactions were carried out on polymers which might at present lack great industrial significance but which nevertheless demonstrate reactive possibilities of macromolecules. Thus Michel and Murphy (*85*) carried out intramolecular rearrangements on polyketones. Also, copolymers of ethylene and carbon dioxide were submitted to the Bechmann and Schmidt rearrangements to form polyamides,



In a similar manner, a poly(*p*-aminostyrene) was prepared from poly(*p*-acetyl styrene) using the Schmidt reaction (*86*).

Mallavarapu and Ravve (*87*) carried out the Wittig reaction on polymers containing aldehydes and ketones to introduce unsaturation into the structures,



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Degradation of Polymers

25

The term *degradation* should imply any number of reactions of polymers, all leading to the loss of desired physical properties. Such reactions can come about by a variety of means, and are obviously a function of the molecular structure and the situation or causative agents which may bring them about. These causative agents can be chemicals, such as moisture, or they can be physical conditions, such as high temperatures, or radiation, and so on, which may lead to bond ruptures or cross-linking or both.

25-1. Hydrolytic Degradation

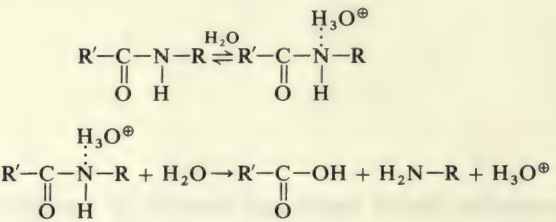
Some polymers exhibit a very noticeable sensitivity to moisture. Most detailed studies of hydrolytic deteriorations were carried out on polyesters and polyamides, although other macromolecules, such as cellulose and its derivatives, received considerable attention.

McMahon and co-workers (*1*) investigated the hydrolytic rate of poly(ethylene terephthalate) films over a wide temperature and humidity range. They found that the degradation was dependent on film thickness, which controlled the diffusion rate of the moisture. Golike and Lasoski (*2*) also studied the rates of hydrolysis and also concluded that the reaction is controlled by the rate of diffusion. This is argued against by Davis and co-workers (*3*), who point out that such an assumption does not take into consideration the reverse reaction, which is esterification occurring at low relative humidity, making the overall measured rate smaller than the true value.

Waters (*4*) studied alkaline hydrolysis of poly(ethylene terephthalate) fiber, using 20% potassium hydroxide solution at 98°C. He concluded that alkaline hydrolysis differs from one taking place under neutral conditions, in that the reaction is not homogeneous with respect to the polymer. The fiber was attacked on the surface only, with resultant loss of weight coming from the glycol and

terephthalate ions, both being removed into solution. And it seemed that formation of negatively charged carboxyl groups on the surface tended to repulse the attacking hydroxyl ions, thereby preventing penetration into the polymer structures.

The acid hydrolysis of polyamides was studied by Myagkov and Pakshver (*5*). They found that in dilute acid hydrolysis of polycaprolactam the reaction rate was dependent upon [lactam][$H_3O^{\oplus}$]. When an excess of an acid was used, however, such as 1.2 *M* of sulfuric acid, [$H_3O^{\oplus}$] changed little during the hydrolysis. So the mechanism was postulated to be



25-2. Thermal Degradation

Thermal degradation of polymers can be divided into two types: random degradation and chain degradation. The first type can be compared to a reverse polycondensation. Rupture takes place at random points along the chain, leaving fragments which can be thought of as being large by comparison to monomer units. The second type is a depolymerization reaction, which involves successive release of monomer units from the chain ends. Such a reaction is the opposite of the propagation step (a depropagation) in addition polymerization. Both reactions may occur simultaneously in a polymer chain, or only one of them may take place exclusively, and they may both be initiated by thermal means and also by ultraviolet light, oxygen, ozone, chemical agents, or radiation.

It should also be borne in mind that the depropagation reaction need not always be initiated at the terminal end of the macromolecule. Instead, imperfections in the chain structure, such as an initiator fragment or a peroxide or an ether link present from polymerization in the presence of oxygen can be a weak link at which depolymerization might initiate.

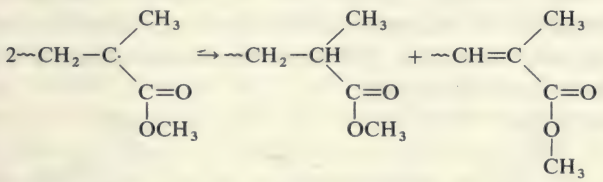
In addition, even a macromolecule possessing no defects in composition may still have weak points, such as a tertiary hydrogen atom of a slightly higher activity, which could be the position for attack.

A large number of addition polymers will depolymerize at elevated temperatures (*6*). The amount of depolymerization and the rate, as well as the resultant product and the number of side reactions which can take place, will vary with individual polymers. For example, poly(methyl methacrylate) can be converted almost quantitatively back to the monomer. Also, depolymerization occurs from the terminal end, with the result that molecular weight decreases slowly

in proportion to volatilization. Polyethylene, on the other hand, decomposes into longer olefinic fragments, actually yielding little monomer. At the same time, the molecular weight decreases rapidly, with only a small amount of volatilization taking place. These two examples represent extremes in behavior. Many other polymers fall between the two.

Studies were carried out on the relationships between polymer structures, their depolymerization rates, and the type of products obtained (*7–13*). It was demonstrated that the mechanism of depolymerization occurs probably by a free-radical mechanism in all addition polymers and that the reactions are quite similar. The differences, however, occur in the relative importance between depropagation and transfer within each individual polymer system. When depropagation assumes a major role during degradation, the molecular-weight reduction is proportional to the formation of monomer, with the rate of depropagation decreasing throughout the reaction. When transfer is significant, however, the molecular weight will decrease rapidly, while little monomer will form, and the volatile products will contain large segments of the chains. The rate of depolymerization will exhibit a maximum.

As stated, the propagation of depolymerization is the reverse of propagation in free-radical polymerization. At some elevated temperature both rates become equal. This is known as "ceiling" temperature. Termination in such a reaction is also similar to polymerization, as it can be terminated through mutual interaction of pairs of radicals,



Furthermore, depropagation of addition polymers could occur even at ordinary temperatures, depending upon formation of some radicals capable of depropagating.

In general, it is agreed that depolymerization is more commonly initiated at the chain end, especially when the end is unsaturated from termination by disproportionation.

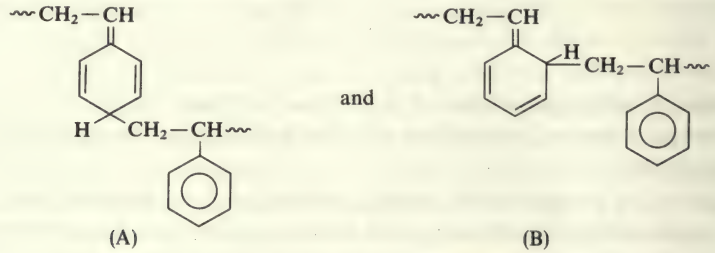
The structure of the polymer itself will determine whether secondary reactions will occur in place of depropagation and to what extent. Thus the nature of the pendant groups on the backbone as well as the bonding forces of these groups will have a bearing on the course of the reaction. If such pendant groups, for instance, will yield hydrochloric acid or acetic acid fairly readily, then the degradation reaction may take this form in preference to depropagation. In addition, the location of substituent groups to each other can influence the location of bond ruptures in depolymerization, for an all head-to-tail structure will obviously rupture differently from one possessing tail-to-tail links. Also,

any cross-linkages present will seriously hamper the progress of depolymerization. Finally, the molecular weight of the polymer appears to have some influence on degradation, as high-molecular-weight species seem to be more prone to degradation.

25-3. Degradation of Polystyrene

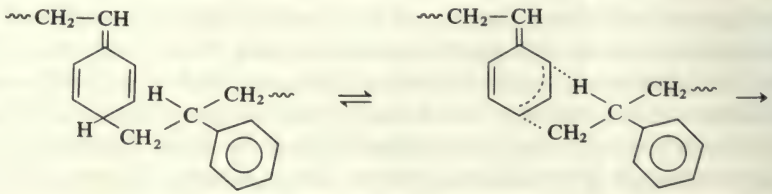
The reactivity of the degrading polymer radical will determine, of course, the path the reaction will take—whether it will be depropagation or transfer. Availability of reactive atoms (labile hydrogens and others) for transferring will also have a bearing. One exception to the above is polystyrene, which will decompose to give a volatile product containing 42% monomer and small amounts of toluene, ethylbenzene, and methylstyrene. The rest of the volatile material is composed of dimers, trimers, and tetramers but no higher fractions. This would suggest that depolymerization proceeds primarily by depropagation. Nevertheless the rate exhibits a maximum, and there is a rapid decline in molecular weight, indicating scission of the chains.

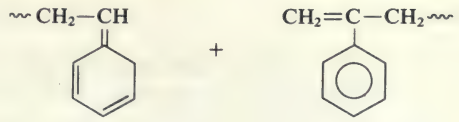
Cameron and Grassie (*14*) presented some evidence that rapid decrease in molecular weight is the result of scission of weak points in the polymer, as suggested by Jellinek (*15–17*), and is independent of the free-radical depolymerization reaction. This was studied further by Grassie and Kerr (*18*), who concluded that some of the weak points could be due to occasional head-to-head addition of styrene units. Also the polystyryl radical is resonance-stabilized. Based on the assumption that the radical center is in the benzene ring, Cameron and Grassie felt (*19*) that some monomer addition could assume structures similar to keteneimines,



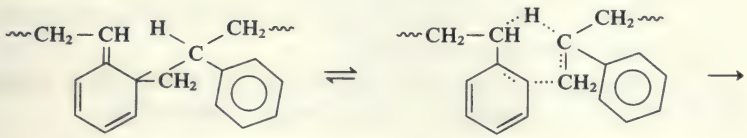
(A) (B)

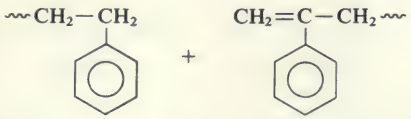
which would be the weak points in the chain. This allowed them to propose the following reaction scheme for chain scission leading to molecules rather than radicals:





or (B),



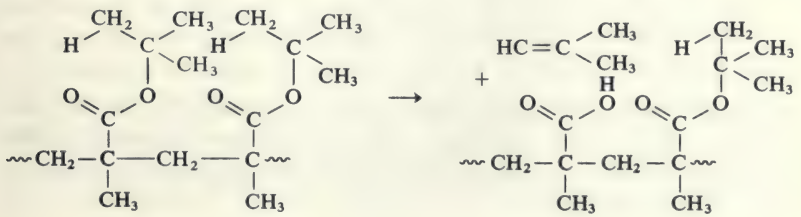


25-4. Decomposition of Polymethacrylates

It was demonstrated by Crawford (*20*) that the polymers from the lower alkyl esters of methacrylic acid will depolymerize thermally at temperatures up to 250°C, with the main product of such depolymerizations being the monomer. Poly(*t*-butyl methacrylate), however, yields isobutene quantitatively instead. Grassie and co-workers (*21–23*) concluded from a study of decomposition of a number of polymethacrylates that actually thermal depolymerization to monomer is probably common to all polymethacrylate esters. However, as the size of the alkyl group is increased, particularly with secondary and tertiary esters, the tendency for the ester group itself to decompose also increases. The products from such ester decompositions interfere with free passage of the depolymerization process along the polymer chains.

In this series the polymers, poly(methyl methacrylate) is unique in that it lacks β-hydrogen atoms. Thus ester decomposition is impossible in this instance, with the result that quantitative yields of monomer are obtained.

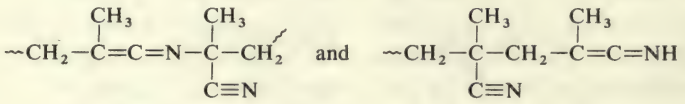
The degradation of poly(*t*-butyl methacrylate), the lowest member of the polymethacrylates which undergoes thermal ester decomposition instead of depolymerization, can be shown as follows:



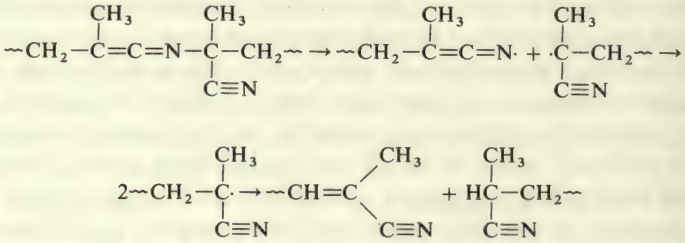
25-5. Nitrile Polymers

Grassie and McNeill (*24–28*) explain thermal degradation of polymethacrylonitrile on the basis of three separate reactions. These three are (1) radical depolymerization, (2) color development, and (3) decomposition of keteneimine structures. The three reactions take place at 20–120°C for (1), 120–220°C for (2), and above 220°C for (3). Reactions (1) and (3) are depolymerization processes, whereas (2) is a non-chain-scission process.

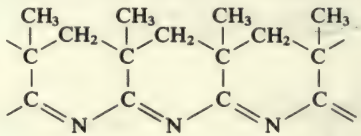
The exact mechanism of keteneimine process is not clear. These structures apparently are produced during free-radical polymerization (*28*),



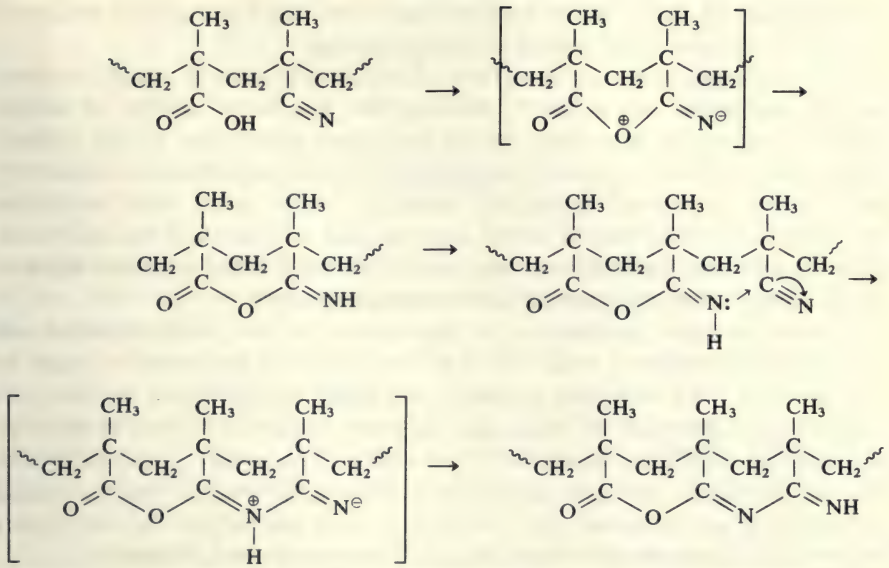
The latter is a very unstable structure. One possible mechanism of the disappearance of keteneimine structures involving molecular weight loss might be by way of scissions of carbon–nitrogen bonds in the chains followed by rearrangements (*28*),



The thermal color formation appears to be caused by an entirely different reaction in the nitrile polymers. Infrared data shows loss of much of the nitrile group and an increase in C=N and conjugated C=N groups (*29–31*). This led to the conclusion that the molecular structure of the colored material is the fused-ring ladder polymer (Chapter 19),



It was also observed that a carboxyl peak had to be present for the polymers to develop color. Such a peak was found to be present due to traces of methacrylic acid units in the polymer chains. This information led to formulation of the following reaction scheme:



The last step leads to long conjugated sequences which are chromophors. It was found that many different nucleophilic agents will tend to initiate this reaction. Polyacrylonitrile was demonstrated to act in an identical manner (*32*).

25-6. Poly(vinyl chloride) and Poly(vinylidine chloride)

Anyone who ever worked with poly(vinyl chloride), whether with a homopolymer or a copolymer, is familiar with the tendency of this material to thermally discolor. The mechanism of this discoloration, which involves loss of HCl, is now more or less understood (*33*).

The thermal reaction is linear with time at temperatures below 130°C, but becomes autocatalytic above it. It was observed (*33*) that this amount of instability at such temperatures cannot be explained alone on the basis of energy relationships required to remove secondary chlorine atoms. This means that other factors must be involved, such as attack from decomposing catalyst residues, weakness due to chain branching, and points of oxidation. Thus the linear reaction at 130°C may possibly proceed from some point of unsaturation, whereas the acceleration at higher temperatures might, perhaps, be due to initiation from less labile structures, such as chain branch points.

Similar reasoning can be applied to photodegradation of poly(vinyl chloride), which would not be expected to be affected by light radiation of wavelength greater than 2350 A, as judged from comparison to behavior of simple alkyl chlorides (*33*). Light of wavelengths greater than 2350 A, however, will degrade poly(vinyl chloride). It must, therefore, be concluded that initiation is the result

of absorption by impurities or perhaps from some small amounts of unsaturation which occurred from loss of HCl in processing.

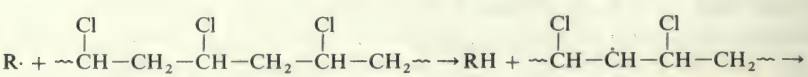
The first suggestion that poly(vinyl chloride) degradation occurs by free-radical mechanism was made by Arlman (*34*). The major portion of radical attack is believed to take place on the methylene rather than on the tertiary hydrogens (*30*). This conclusion was reached by observing behavior of relatively heat stable chlorinated poly(vinyl chloride) which lacks such methylene hydrogens (*31*). Once radical attack occurred and unsaturation was produced, then the adjacent methylene groups to the liberated chlorine atoms become allylic and, therefore, possessing labile hydrogen atoms.

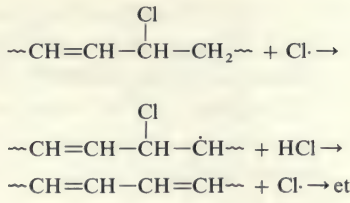
A more extensive mechanism for degradation of poly(vinyl chloride) was proposed by Stromberg et al. (*31*). The initiation was proposed to occur by scission of a C—Cl bond. The weaker C—Cl bonds and, therefore, the first ones to rupture will probably be those adjacent to double bonds formed by termination through disproportionation or by transfer to monomer. This mechanism (*31*) does not imply, however, that initiation necessarily occurs at such a terminal end, rather at any monomer unit. As a result, such a mechanism does not appear to answer all the questions about degradation of poly(vinyl chloride).

Furthermore, the role of HCl in poly(vinyl chloride) degradation is still subject to controversy. It was first believed that HCl catalyzed the reaction. This was shown not to be the case (*30,34*).

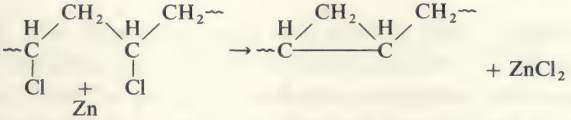
So it is now suspected that poly(vinyl chloride) degradation of a pure polymer is initiated at an unsaturated terminal chain structure formed by transfer during polymerization. In an impure polymer, however, initiation can occur from a labile structure. Also, chlorines adjacent to branch points can be liberated at elevated temperatures. Unsaturated structures are also capable of absorbing light and then returning to the ground state by liberating adjacent chlorine atoms. After the reaction was initiated by one of these processes, it can be propagated from one unit to another along the chain, ultimately resulting in conjugated structures (*35*).

To sum up, the work by Fuchs and Louis (*29*) indicates that radical attack occurs on a methylene hydrogen atom preferentially. This produces a labile chlorine atom in a beta position which is then released to stabilize the structure. The newly formed free chlorine radical abstracts a proton from another methylene group, thereby in turn producing the next labile chlorine atom. Probability is great that each chlorine radical will attack the nearest methylene group. And, because the nearest one is also allylic, its abstraction should be highly favored. So, a chain reaction is started and perpetuated, leading very likely to conjugated structures. Such conjugated structures with sufficient number of double bonds should be colored. The overall reaction can be written as follows:

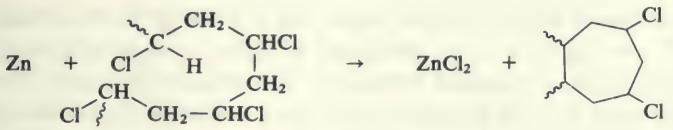




A different type of poly(vinyl chloride) degradation takes place in the presence of zinc. Here cyclopropane rings are formed at a high rate via removal of 1,3-dichloride units (*36*),

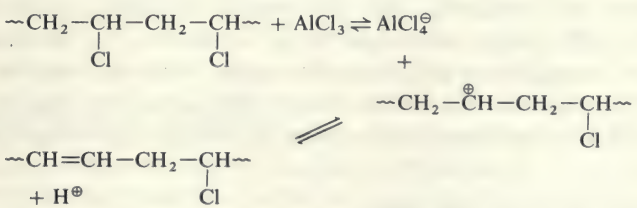


Larger rings, such as cyclopentane and cycloheptane, are possible (*37*) but at a slower rate. When chlorine atoms are isolated, however, between two cyclopropane rings, steric factors prevent them from participating in larger ring formation,

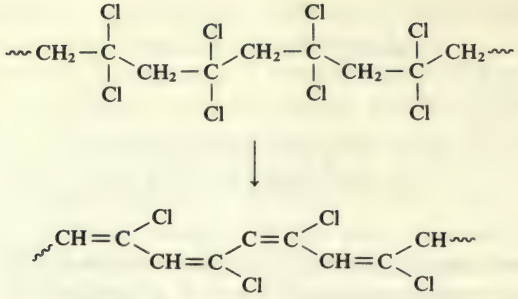


The reaction lasts a long time, reaching completion in 150–200 hours. In some cases of vinyl chloride–vinyl acetate copolymers, reaction may not level off before 400 hours (*38*).

Dehydrochlorination of poly(vinyl chloride) with Lewis acids such as aluminum chloride is enhanced by presence of vicinal dihalide units in the structure (*39,40*),

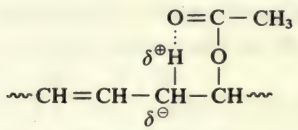


Poly(vinylidine chloride) was investigated by Boyer (*41*). The conclusion was that a conjugated system results in a similar manner,



25-7. Poly(vinyl acetate)

Thermal cleavage of ester groups into carboxylic acids and olefins is well established (*6,41,42*). The reaction proceeds by molecular mechanism facilitated by a six-membered ring interaction capable of existing between the β-hydrogen atom of the alcohol residues and the carboxyl group. Any adjacent double bond will activate the methylene groups through electron attraction,



This results in loss of acetic acid and formation of another double bond, which, in turn, facilitates the loss of the next acid molecule as a propagating step in formation of colored, conjugated structures. The reaction proceeds over a long period of time with the rate accelerating as more and more chains are initiated. The loss of acid is the only significant product at temperatures up to 200–250°C. Beyond this temperature, however, poly(vinyl acetate) [and, incidentally, poly(vinyl chloride) as well] will form benzene and other aromatic compounds among their volatile products.

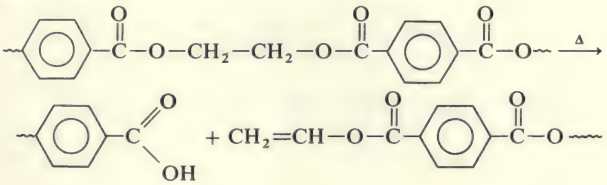
25-8. Polytetrafluoroethylene

Lewis and Naylor (*43*) investigated thermal degradation of polytetrafluoroethylene and concluded that the reaction products consist mainly of monomer, a dimer, and a compound of the formula C_4F_6. The ratio of these materials are dependent upon the pressure under which the reaction is carried out. Under high-vacuum conditions, almost 100% monomer may be obtained (*44*). This indicates that degradation occurs by a typical depropagation process.

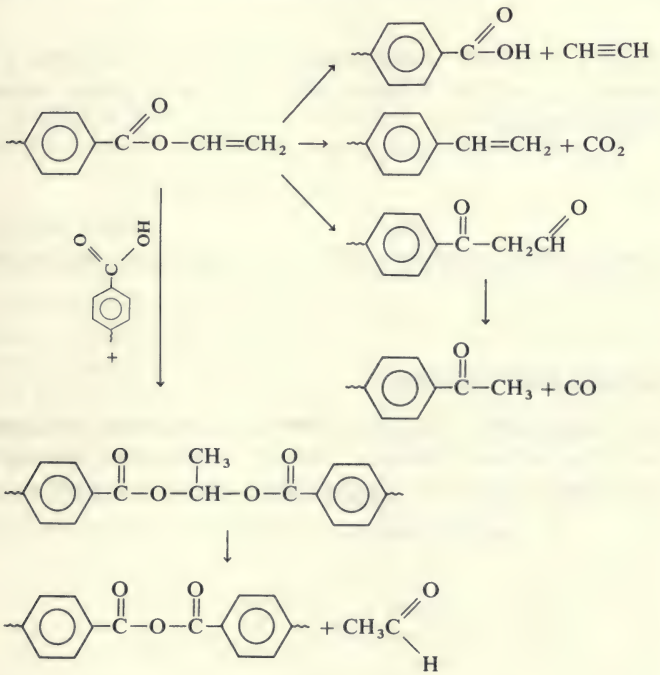
25-9. Poly(ethylene terephthalate)

Decomposition of poly(ethylene terephthalate) was studied by Ritchie at 282–323°C and by Goodings at 440–450°C (*6a*). The major products of

degradation are carbon dioxide, acetaldehyde, and terephthalic acid. Also in trace amounts are anhydrides, benzoic acid, *p*-acetylbenzoic acid, acetophenone, vinyl benzoate, water, methane, ethylene, acetylene, and some ketonic substances. After studying some model compounds, the investigators concluded that the mechanism of degradation is random, the initial step resulting in scissions which leads to carboxyl and vinyl groups,

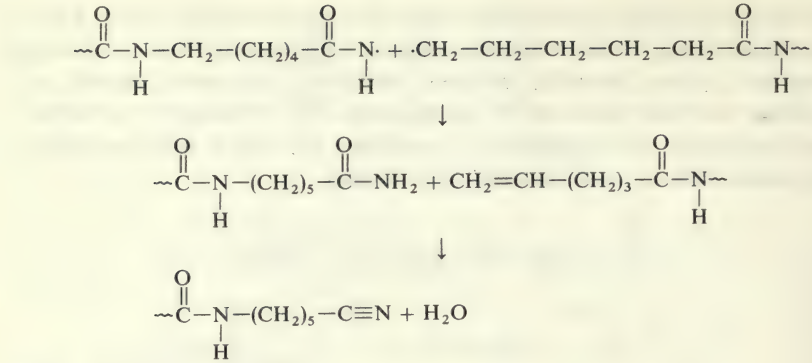


The vinyl end groups then decompose in a number of ways:

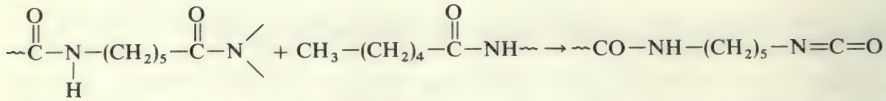


25-10. Degradation of Polyamides

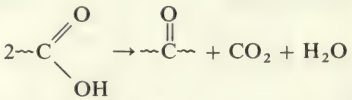
Degradation of polyamides was studied quite thoroughly by Kamerbeek and co-workers (*6b*). They conclude that at least in nylons 6 and 6-6, the degradation at processing temperatures can be separated into primary and secondary processes. The primary ones consist of homolytic scissions at the nitrogen carbon bond, as in polycaprolactam:



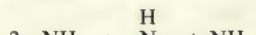
and



The secondary processes would consist of amide hydrolysis from water present followed by reaction of two carboxyl groups to yield a ketone, carbon dioxide, and more water,

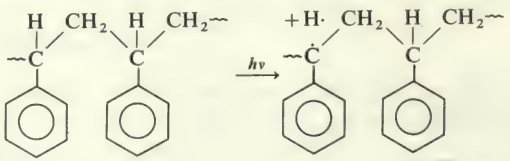


and two primary amine groups to yield a secondary amine and ammonia,

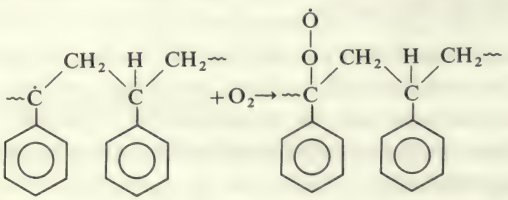


25-11. Oxidative Bulk Degradation

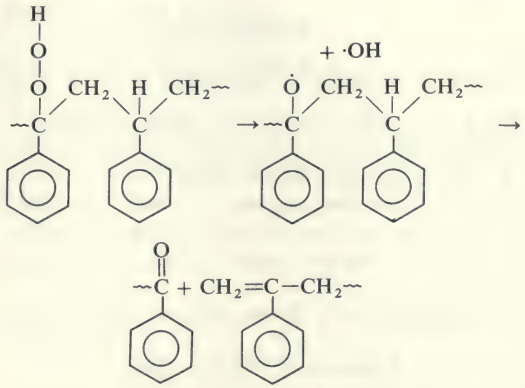
This type of degradation also takes place via a free-radical mechanism. Such reactions are often initiated when a hydrogen is discarded through a photoreaction. Oxidative degradation of polystyrene would be a good example,



The styrene radical is now subject to attack by oxygen, resulting in formation of a peroxy radical,



The peroxy radical will abstract a proton from some other labile position, thereby forming hydroperoxides and a new radical sight. The newly formed hydroperoxide groups is subject to decomposition, ultimately resulting in chain cleavage into ketones and olefins,

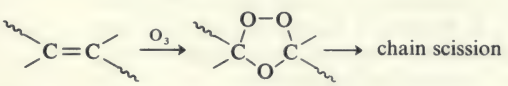


So the oxidative process can be separated into two steps: (1) formation of hydroperoxides, and (2) decomposition of these hydroperoxides.

25-12. Ozone Attack

Ozone is one of the prime causes for deterioration of many polymers, particularly elastomers. Thompson (*45*) was first to observe that ozone generated in the laboratory caused cracking of stretched rubber. Williams (*46*) pointed out that the direct attack by the ozone in the atmosphere on rubber items was responsible for development of cracks. The subject received much attention and was thoroughly investigated. This was discussed in three review articles (*47–49*).

Chemically, the attack by ozone is through a reaction with olefinic bonds in the well-known manner of ozone reacting with olefins,



25-13. Degradation by Radiation

The major effect of radiation on macromolecules (*50*) is chain scission usually occurring on 1,1-disubstituted structures, such as poly(methyl methacrylate), polyisobutylene, or poly(α-methylstyrene). Similar effects occur in halogen-bearing polymers, such as poly(vinyl chloride), poly(vinylidine chloride), and polytetrafluoroethylene. The tendency to degrade has been explained on the basis of presence of tertiary hydrogen atoms which are weaker than average

carbon-to-carbon bonds and, therefore tend to rupture. In their absence, it was blamed on unusually strong bonds (such as C—F) elsewhere in the molecule (*50*). Shultz (*51*) points out that our understanding of the processes which initiates these reactions should be made clearer.

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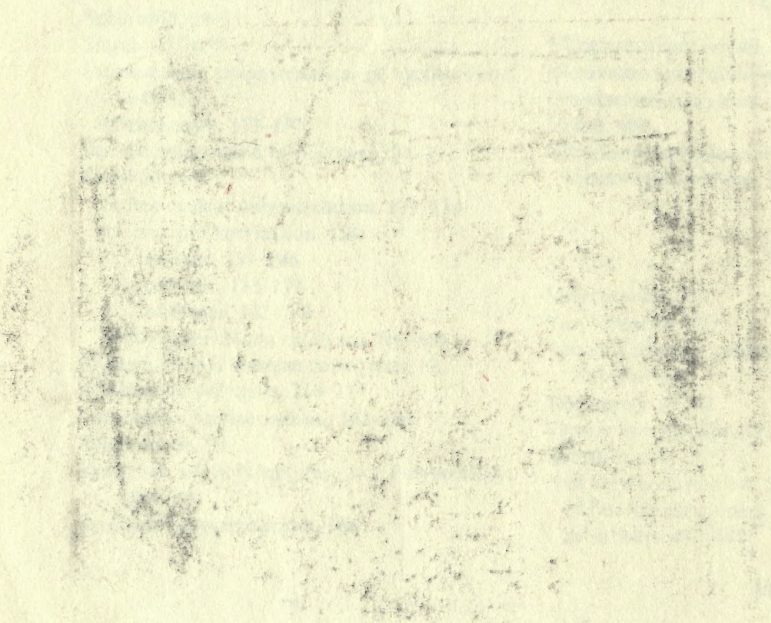

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